Solutions of Exercises in “An Introduction to Dynamics of Colloids”

Jan Karel George Dhont, Kyongok Kang

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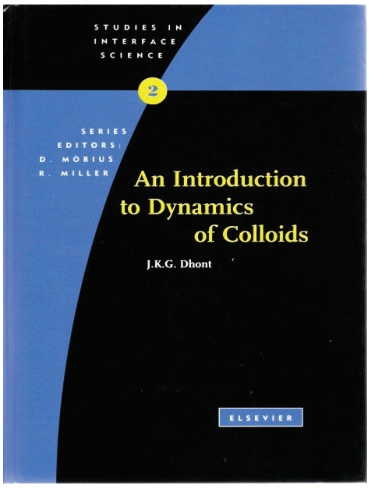

PREFACE

This solution book provides solutions to exercises of the book of J.K.G. Dhont "An Introduction to Dynamics of Colloids" as published in the Interface Science Series, vol II, Elsevier press, 1996. As mentioned in the preface in the book, colloid science is the domain of both chemists and (theoretical) physicists. The first chapter in the book is therefore aimed to provide a minimum mathematical background for those who did not have a sufficient mathematical training. A single chapter can of course not fully cover this gap in the mathematical background between experimentalists and theoreticians, and might render the exercises still problematic for those who are not used to work with equations.

The aim of this solution book is to bridge this gap, by providing the mathematics needed to solve the exercises in detail. We tried to give the solutions in a way that it is also accessible for those who are less trained in mathematics. Every step is worked out in detail. Some times we added remarks on the interpretation and physical implications of results. In this solution book, exercises are selected that are not purely concerned with mathematics, but where rather the understanding of physics is the aim. We hope that this exercise book will lower a possible activation energy concerned with the mathematics involved in exercises.

The content of the book is focused on equations of motion for Brownian systems (in particular the Smoluchowski equation), hydrodynamics, light scattering, diffusion, sedimentation, critical phenomena, and phase separation kinetics. The effects of simple shear flow on various phenomena are presented throughout the various chapters.

Some of the original figures in the book are re-arranged for illustration whenever helpful within the context of an exercise. We also added some text to further explain the physics on an intuitive level, and mentioned some typos in the book whenever relevant within an exercise.

We sincerely hope that you enjoy solving the exercises with the help of this solution book.

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June-July, 2013
Forschungszentrum Juelich,
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Exercises Chapter 1: INTRODUCTION


Looking down view of the surroundings at Les-Houches, France

1.1 The sedimentation velocity of a colloidal sphere in very diluted suspensions is equal to,

$$\vec{v}_S^0 = \frac{1}{6\pi\eta_0 a}\vec{F}^{ext}$$

where η_0 is the shear viscosity of the solvent, and $\vec{F}^{ext}$ the external force acting on the colloidal sphere with a radius a. The gravitational external force, corrected for buoyancy, is equal to (with ρ_f the specific mass of the colloidal particle, and ρ_p that of the solvent fluid)

$$\vec{F}^{ext} = \vec{g}\,\frac{4\pi}{3}a^3(\rho_p - \rho_f)$$

The question is what the maximum size of a colloidal particle (silica) in water can be, such that the particle displacement due to sedimentation is not larger than its own radius, **during an experiment of 1 sec**. For the calculation, use that the viscosity of water is 0.001 g/ml, the specific mass of water is 1.0 Ns/m^2 and that of amorphous silica particle is ~ 1.8 g/ml .

The gravitational force acceleration constant is $|\vec{g}| = 9.8\, m/s^2$.

Substitution gives,

$$\vec{v}_S^0 = \frac{1}{6\pi\eta_0 a}\vec{F}^{ext} = \frac{1}{6\pi\eta_0 a}\left(g\frac{4\pi}{3}a^3\left(\rho_p - \rho_f\right)\right)$$

The time during which sedimentation takes place over a distance equal to a is,

$$t = 1[s] = \frac{a}{|\vec{v}_s^{\,0}|}$$

Hence

$$|\vec{v}_s^{\,0}| = \frac{a}{1[s]} = \frac{1}{6\pi\eta_0 a}\vec{F}^{ext} = \frac{1}{6\pi\eta_0 a}\left(g\frac{4\pi}{3}a^3\left(\rho_p - \rho_f\right)\right)$$

So that, putting in numbers

$$\frac{a}{1[s]} = \frac{2*9.8[m/s^2]*a^3[m^3]*\left(0.8*10^{-3}[kg/(cm)^3]\right)}{3*3*\left(0.001[Ns/m^2]\right)*a[m]},$$

Solving for a thus gives

$$a = \frac{9*0.001}{2*9.8*0.8*10^{-3}*10^6}\ [m]$$

$$= 0.574*10^{-6}\ [m] \simeq 574\ \ nm$$

Thus, the maximum size that the particle may have in order to sediment at most its own radius during 1 s. is equal to 574 nm.

For higher concentrations, where particles interact through a (effective) hard-core potential, instead of using the free mobility, one might use eqn. (7.90) for the mobility instead.

Jan Dhont indicated that there is an error in this exercise; the time of 1 min, as stated in the book, should be 1 sec.

1.9 Interaction of two charged colloidal spheres (depicted in Fig. 1.1(a))

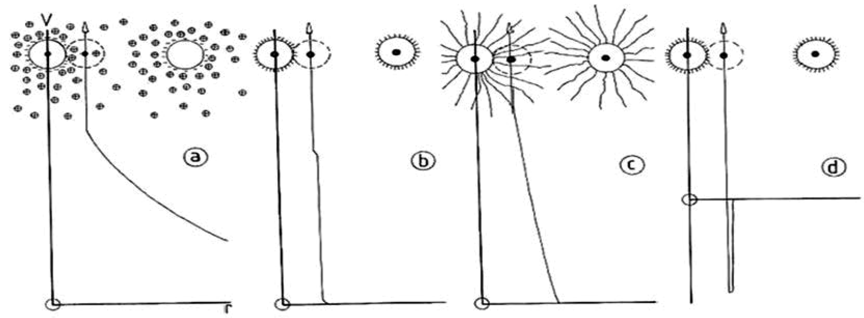


Fig. 1.1: The most common kinds of pair-interaction potentials for spherical colloidal particles: (a) the screened Coulomb potential (which will be treated in this exercise), that is the DLVO potential with negligible van der Waals attraction, (b) an almost ideal hard-core interaction, (c) steric repulsion of long polymers in a good solvent, where the polymers are grafted to the particle's surface, (d) short-ranged attraction of colloids grafted with polymers in a marginal solvent.

(a) Consider a small charged colloidal particle, located at the origin, in a solvent that contains free ions. The electrostatic potential $\Phi(\vec{r})$ is related to the free charge density $\rho(\vec{r})$ by Poisson's equation as

$$\nabla^2\Phi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon}$$

where ε is the dielectric constant of the solvent, which, for simplicity, is assumed to be the same as the colloidal particle.

The charge density is composed of two terms; one is from the colloidal particle at the origin $Q\,\delta(\vec{r})$ and the other is from the solvent that may have unequal locally unequal ion concentrations $\rho_S(\vec{r})$.

Then

$$\nabla^2\Phi(\vec{r}) = -\frac{\rho_S(\vec{r})}{\varepsilon} - \frac{Q}{\varepsilon}\delta(\vec{r})$$

For simplicity, the colloidal particle is regarded as a point-like, as mathematically described by the delta function. The ion concentrations ρ_j are related to the electrostatic potential by (assuming of point-like ions)

$$\rho_j(\vec{r}) = \rho_j^0 \exp\left(-\beta e z_j \Phi(\vec{r})\right)$$

with ρ_j^0 the number density of that species outside the double layer, where the electrostatic potential $\Phi(\vec{r})$ is zero. The local electrostatic energy of ions of species j is equal to $ez_j\Phi(\vec{r})$, which is the energy in the electrostatic field generated by the remaining ions and the colloidal particle.

The resulting *non-linear Poisson-Boltzmann equation*

$$\nabla^2\Phi(\vec{r}) = -\frac{1}{\varepsilon}\sum_j ez_j\rho_j^0 \exp\left(-\beta ez_j\Phi(\vec{r})\right) - \frac{Q}{\varepsilon}\delta(\vec{r})$$

cannot be solved analytically. For sufficiently small potentials (where $ez_j\Phi(\vec{r})$ is small compared to k_BT), however, we can linearize the above equation.

Note that this is always true for large distances from the colloid, and is only true for *all* distances whenever the surface potential is sufficiently small.

Also due to electroneutrality, $\sum_j ez_j\rho_j^0 = -\frac{Q}{V} \approx 0$ for large volumes of the system.

Linearization leads to the so-called *linear Poisson-Boltzmann equation*

$$\nabla^2\Phi(\vec{r}) = \kappa^2\Phi(\vec{r}) - \frac{Q}{\varepsilon}\delta(\vec{r}),$$

$$\kappa = \sqrt{\frac{e^2\sum_j z_j^2\rho_j^0}{k_BT\varepsilon}},$$

$$\Phi(\vec{r}) = \frac{Q}{4\pi\varepsilon}\frac{\exp\left(-\kappa r\right)}{r}$$

This can be seen as follows

$$\rho_s = \sum_j ez_j\,\rho_j^0 \exp\left(-\beta ez_j\Phi(\vec{r})\right) \simeq \sum_j ez_j\,\rho_j^0\left(1-\beta ez_j\Phi(\vec{r})\right)$$

$$\begin{aligned}\frac{\rho_s}{\varepsilon} &\simeq \sum_j ez_j\frac{\rho_j^0}{\varepsilon}\left(1-\beta ez_j\Phi(\vec{r})\right)\\ &= \sum_j ez_j\frac{\rho_j^0}{\varepsilon} - \sum_j\frac{\rho_j^0}{\varepsilon}\beta\left(ez_j\right)^2\Phi(\vec{r}) = 0 - \sum_j\frac{\rho_j^0}{\varepsilon}\beta\left(ez_j\right)^2\Phi(\vec{r})\end{aligned}$$

which is valid for

$$\left|\beta ez_j\Phi(\vec{r})\right| = \left|\frac{ez_j\Phi(\vec{r})}{k_BT}\right| \ll 1$$

It is convenient to use Fourier Transformation to solve the linearized *Poisson-Boltzmann equation* (see exercise 1.5)

$$k^2\,\Phi\left(\vec{k}\right)+\kappa^2\,\Phi\left(\vec{k}\right)=\frac{Q}{\varepsilon}$$

Fourier inversion thus leads to

$$\Phi\left(\vec{r}\right)=\frac{Q}{\left(2\pi\right)^3\,\varepsilon}\int d\vec{k}\,\frac{e^{i\vec{k}\bullet\vec{r}}}{k^2+\kappa^2}=\frac{Q}{\left(2\pi\right)^3\,\varepsilon}\int_0^{\infty} dk\,\frac{k^2}{k^2+\kappa^2}\oint d\hat{k}\,e^{i\vec{k}\bullet\vec{r}}$$

Using the identity, where the angular integration are performed explicitly,

$$\oint d\hat{k}\,e^{i\vec{k}\bullet\vec{r}}=\int_0^{2\pi} d\phi\int_0^{\pi} d\theta\sin\theta\,e^{i\vec{k}\bullet\vec{r}}=2\pi\int_{-1}^{1} dx\,e^{ikrx}=\frac{2\pi}{ikr}\left(e^{ikr}-e^{-ikr}\right)$$

it is found that

$$\Phi\left(\vec{r}\right)=\frac{Q}{8\pi^2\varepsilon\,ir}\int_{-\infty}^{\infty} dk\,\frac{k}{k^2+\kappa^2}\left(e^{ikr}-e^{-ikr}\right)$$

From the residue theorem it is found that

$$\int_{-\infty}^{+\infty} dz\,\frac{z}{\left(z+i\kappa\right)\left(z-i\kappa\right)}e^{\pm ikr}=\pm\pi i\,e^{-\kappa r}$$

so that it is finally found that the electrostatic potential is equal to

$$\boxed{\Phi\left(\vec{r}\right)=\frac{Q}{4\pi\varepsilon}\frac{e^{-\kappa r}}{r}}\qquad\text{with}\qquad\boxed{\kappa\equiv\sqrt{\frac{e^2\sum_j z_j^2\rho_j^0}{k_BT\,\varepsilon}}}$$

the inverse Debye-screening length.

(b) The Helmholtz free energy of a system of two particles and the free ions in the solvent is the colloid-colloid pair-interaction potential. The pair-interaction force between the two colloidal particles is $\vec{F}=-\nabla\left[U-T\,S\right]$, where U is the potential energy and S the entropy of free ions in solution. Within the linearization approximation discussed in (a), for particles with a given, fixed charge Q , the total electrostatic potential is the sum of each of the separate colloidal particles

$$\Phi_t(\vec{r})=\Phi\left(\left|\vec{r}-\vec{R}_1\right|\right)+\Phi\left(\left|\vec{r}-\vec{R}_2\right|\right)$$

where $\vec{R}_{1,2}$ are the position coordinates of the colloidal particles.

The local electrostatic energy density is equal to $\frac{1}{2}\varepsilon\left|\nabla\Phi_t(\vec{r})\right|^2$, so that the total electrostatic energy can be written equally both in real space and Fourier space as (see Exercise 1.4b)

$$U=\frac{1}{2}\varepsilon\int d\vec{r}\left|\nabla\Phi_t(\vec{r})\right|^2=\frac{\varepsilon}{2(2\pi)^3}\int d\vec{k}k^2\left|\nabla\Phi_t(\vec{k})\right|^2$$

For the non-interacting ions, the entropy is

$$S=-k_B\int d\vec{r}_1...\int d\vec{r}_M P(\vec{r}_1,...,\vec{r}_M)\ln\left(P(\vec{r}_1,...,\vec{r}_M)\right)$$

where the probability distribution function (pdf) is equal to

$$P(\vec{r}_1,...,\vec{r}_M)=\frac{\exp\left(-\beta\sum_{j=1}^{M}ez_j\Phi_t(\vec{r}_j)\right)}{Q(N_1,...,N_m,V,T)}$$

with the configurational partition function equal to

$$Q(N_1,...,N_m,V,T)=\int d\vec{r}_1...\int d\vec{r}_M\exp\left(-\beta\sum_{j=1}^{M}ez_j\Phi_t(\vec{r})\right)$$

Expansion the entropy up to quadratic order in the assumed small quantity $\frac{ez_j\Phi(\vec{r})}{k_BT}$

thus leads to

$$S=\frac{k_B}{V^M}\left\{V^M\ln\left(V^M\right)+\frac{1}{2}\frac{I_1^2}{V^M}-\frac{1}{2}I_2\right\},$$

$$I_i=\int d\vec{r}_1...\int d\vec{r}_M\left(\beta\sum_{j=1}^{M}ez_j\Phi_t(\vec{r}_j)\right)^i,\quad i=1,2$$

This can be seen from (here Q is not the colloid charge, but the partition function)

$$\begin{aligned}S&=-k_B\int d\vec{r}_1...\int d\vec{r}_M P(\vec{r}_1,...,\vec{r}_M)\ln\left(P(\vec{r}_1,...,\vec{r}_M)\right)\\&=-k_B\int d\vec{r}_1...\int d\vec{r}_M\frac{e^{-\beta\Sigma}}{Q}\left(-\beta\Sigma-\ln Q\right),\\Q&=V^M-\beta\Sigma d\vec{R}+\frac{1}{2}\beta^2\int d\vec{R}\,\Sigma^2+\cdots,\qquad V^M\equiv\int d\vec{r}_1...\int d\vec{r}_M\end{aligned}$$

by using the expansions

$$\exp(x)\approx 1+x+\frac{1}{2}x^2,\quad \frac{1}{1-x}\approx 1+x+x^2,\ and\quad \ln(1-x)\approx -x-\frac{1}{2}x^2$$

Since we are interested in the change of the entropy with the relative position of the colloidal particles, i.e., $\vec{R}_1 - \vec{R}_2$, the thermodynamic entropy term $V^M \ln\left(V^M\right)$ can be omitted.

Furthermore since $\int d\vec{r}_j \Phi_t(\vec{r}_j)$ is a constant, it is also does not contribute to the pair-interaction force.
Therefore the relevant entropy is

$$-T\,S = \frac{1}{2}\varepsilon\,\kappa^2 \int d\vec{r}\,\Phi_t^2(\vec{r}) = \frac{\varepsilon\,\kappa^2}{2\,(2\pi)^3}\int d\vec{k}\left|\Phi_t(\vec{k})\right|^2$$

The pair-interaction potential is thus equal to

$$V\left(\left|\vec{R}_1 - \vec{R}_2\right|\right) = U - T\,S = \frac{\varepsilon}{2\,(2\pi)^3}\int d\vec{k}\left(k^2 + \kappa^2\right)\left|\Phi_t(\vec{k})\right|^2$$

From the Fourier transform of the linearized solution of the Poisson-Boltzmann equation in (a), it is found that

$$\begin{aligned}\Phi_t(\vec{k}) &= \frac{Q}{\varepsilon}\left(e^{i\vec{k}\cdot\vec{R}_1} + e^{i\vec{k}\cdot\vec{R}_2}\right)\frac{1}{k}\frac{1}{2i}\int_0^\infty dr e^{-\kappa r}\left(e^{ikr} - e^{-ikr}\right)\\ &= \frac{Q}{\varepsilon}\left(e^{i\vec{k}\cdot\vec{R}_1} + e^{i\vec{k}\cdot\vec{R}_2}\right)\frac{1}{k^2 + \kappa^2}\end{aligned}$$

The pair-interaction potential for electrostatic interactions through double-layer overlap is equal to

$$\boxed{\begin{aligned}V\left(\left|\vec{R}_1 - \vec{R}_2\right|\right) &= \frac{Q^2}{\varepsilon}\frac{1}{(2\pi)^3}\int d\vec{k}\,\frac{e^{i\vec{k}\cdot\left(\vec{R}_1 - \vec{R}_2\right)}}{k^2 + \kappa^2}\\ &= \frac{Q^2}{4\pi\varepsilon}\frac{e^{-\kappa\left|\vec{R}_1 - \vec{R}_2\right|}}{\left|\vec{R}_1 - \vec{R}_2\right|}\end{aligned}}$$

Where the integration is performed using the residue theorem. This is the screened Coulomb or Yukawa potential.

> Note that we assumed that the charge of the colloids is independent of their separation. This is strictly true when the degree of ionization of the chemical groups on the surfaces of the colloidal particles is close to 100%. For partial ionization, the local electrostatic potential affects the ionization equilibrium and thereby the charge on the colloidal particles. Then the appropriate condition is a constant surface potential rather than a constant charge.

1.11 The effective interaction potential

The effective interaction potential $V^{eff}(r)$ is defined, for isotropic and homogeneous systems, which are both translational and rotational invariant, as

$$g(r) = \exp\left(-\beta V^{eff}(r)\right)$$

where $g(r)$ is the pair-correlation function. In this exercise, it is shown that the gradient of this effective potential with respect the distance r between two colloids is equal to the interaction force between the two colloids, averaged over the positions of the remaining colloidal particles.

From the definition of the pair-correlation function of $g(r)$

$$P(\vec{r}_1,\vec{r}_2) \triangleq P(\vec{r}_1)P(\vec{r}_2)g(\vec{r}_1,\vec{r}_2) = \int d\vec{r}_3 \cdots \int d\vec{r}_N \, P_N(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)$$

$$P_N(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N) = \frac{e^{-\beta\phi}}{Q}$$

and where

$$P_1(\vec{r}) = \frac{1}{V}$$

is the one-particle pdf for a homogeneous system.

Then the pair-correlation function becomes

$$\begin{aligned} g(\vec{r}_1,\vec{r}_2) &= V^2 \int d\vec{r}_3 \cdots \int d\vec{r}_N \, P_N(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N) \\ &= V^2 \frac{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta\phi}}{Q} \triangleq e^{-\beta V^{eff}} \end{aligned}$$

Now the effective potential can be expressed in terms of the volume and partition function as

$$-\beta V^{eff}(\vec{r}_1,\vec{r}_2) = 2\ln V - \ln Q + \ln\left(\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta\phi}\right)$$

where the 1st and 2nd terms are independent of the position $\vec{r}_1$ and $\vec{r}_2$.
Thus with a space differentiation with respect to $\vec{r}_1$ gives

$$-\nabla_1 V^{eff}(\vec{r}_1,\vec{r}_2) = +k_B T \; \nabla_1 \ln\left(\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)}\right)$$

$$= \frac{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, \left[-\nabla_1\phi\right] e^{-\beta\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)}}{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)}}$$

Dividing both the numerator and denominator with the partition function Q gives

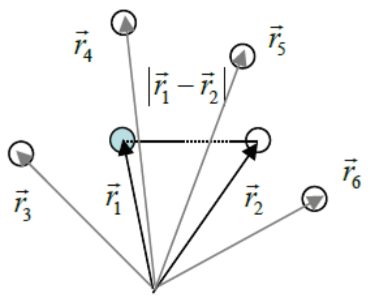
$$-\nabla_1 V^{eff}(\vec{r}_1,\vec{r}_2) = \frac{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, [-\nabla_1\phi] e^{-\beta\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)} / Q}{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, e^{-\beta\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)} / Q}$$

$$= \frac{\int d\vec{r}_3 \cdots \int d\vec{r}_N \, [-\nabla_1\phi] P_N(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)}{P(\vec{r}_1,\vec{r}_2)}$$

$$= \int d\vec{r}_3 \cdots \int d\vec{r}_N \, [-\nabla_1\phi] \frac{P_N(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N)}{P(\vec{r}_1,\vec{r}_2)}$$

$$= \int d\vec{r}_3 \cdots \int d\vec{r}_N \, [-\nabla_1\phi] \, P_c\left(\vec{r}_3,\vec{r}_4,\cdots,\vec{r}_N \middle| \vec{r}_1,\vec{r}_2\right)$$

Here the $P_c\left(\vec{r}_3,\vec{r}_4,\cdots,\vec{r}_N \middle| \vec{r}_1,\vec{r}_2\right)$ is so-called the conditional probability distribution function of the particle coordinates $\vec{r}_3,\vec{r}_4,\cdots,\vec{r}_N$, for given positions of particles, 1 and 2.



Therefore $-\nabla_1 V^{eff}$ is the force that particle 2 exerts on particle 1, averaged over the position coordinates of all other particles, 3, …, N.

1.12 The pair-correlation function $g(r)$ for hard spheres

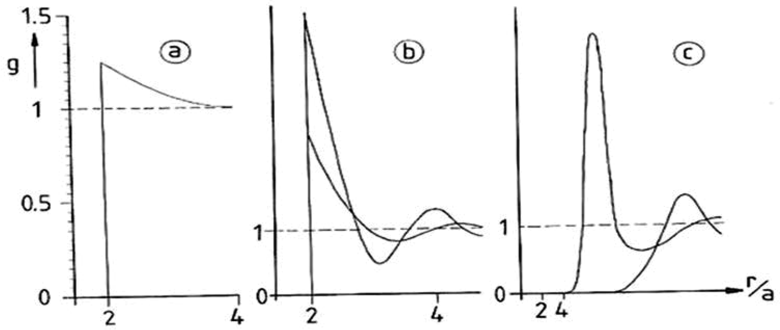


Fig. 1.10 (a) The pair-correlation function to first order in concentration for hard-spheres,

$$g_{hs}(r) = g_0(r) + \bar{\rho} g_1(r) = \begin{cases} 1, & r \geq 4a \\ 1 + \varphi\left[8 - 3\left(\frac{r}{a}\right) + \frac{1}{16}\left(\frac{r}{a}\right)^3\right], & 2a \leq r < 4a \\ 0, & r < 2a \end{cases}$$

with $\varphi = 0.1$, (b) a sketch for hard-spheres at larger concentrations, and (c) for charged spheres with a long-ranged repulsive pair-interaction potential.

The hard sphere pair-interaction potential $V_{hs}(r)$ is defined as with a , radius of the hard core.

$$V_{hs}(r) = \begin{cases} 0, & r \geq 2a \\ \infty, & r < 2a \end{cases}$$

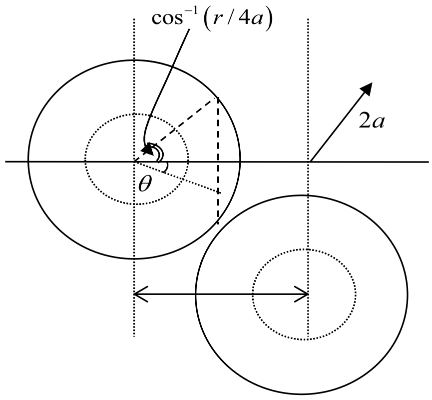
Using the definition of the Mayer-function

$$f_{hs}(r) \equiv e^{-\beta V_{hs}(r)} - 1 = 0, \quad for\ r \geq 2a,$$
$$= -1, \quad for\ r < 2a.$$

it can be verified that

$$\int d\vec{r}_3 f\left(|\vec{r}_1 - \vec{r}_3|\right) f\left(|\vec{r}_2 - \vec{r}_3|\right) = 2\int_0^{2\pi} d\phi \int_0^{\cos^{-1}(r/4a)} d\theta \int_{(r/2)\cos\theta}^{2a} dR\, R^2 \sin\theta$$

$$= 4\pi \int_{r/4a}^{1} dx \int_{(r/2)x}^{2a} dR\, R^2 = \frac{4\pi}{3} a^3 \left[8 - 3\left(\frac{r}{a}\right) + \frac{1}{16}\left(\frac{r}{a}\right)^3\right], \quad for \quad r < 4a$$



To see this, we can use the spherical coordinate system as depicted above

$$
\begin{aligned}
&2\int_0^{2\pi} d\phi \int_0^{\cos^{-1}(r/4a)} d\theta \int_{(r/2)\cos\theta}^{2a} dR\, R^2 \sin\theta = -4\pi \int_1^{r/4a} dx \int_{r/2x}^{2a} dR\, R^2 \\
&= 4\pi \int_{r/4a}^{1} dx \left(\frac{1}{3} R^3 \Big|_{R=r/2x}^{R=2a} \right) = \frac{4\pi}{3} a^3 \left[8 - 2\left(\frac{r}{a}\right) - \frac{1}{8}\frac{r^3}{a^3}\frac{1}{2}\left(-1 + \frac{(4a)^2}{r_2} \right) \right] \\
&= \frac{4\pi}{3} a^3 \left[8 - 3\left(\frac{r}{a}\right) + \frac{1}{16}\left(\frac{r}{a}\right)^3 \right]
\end{aligned}
$$

Then the pair-correlation function for hard spheres for low concentrations is (see eqn. (1.56))

$$
g_{hs}(r) = g_0(r) + \bar{\rho} g_1(r) = \begin{cases} 1, & r \geq 4a \\ 1 + \varphi\left[8 - 3\left(\frac{r}{a}\right) + \frac{1}{16}\left(\frac{r}{a}\right)^3 \right], & 2a \leq r < 4a \\ 0, & r < 2a \end{cases}
$$

This function is displayed and plotted in the above figure, Fig. 1.10 (a) from the book.

1.13 Number density fluctuations

A measure for the amplitude of the fluctuations of the microscopic density is its standard deviation

$$\sigma^2(\vec{r},\vec{r}\,') \equiv \left\langle \left[\rho_m(\vec{r}) - \left\langle \rho_m(\vec{r})\right\rangle\right]\left[\rho_m(\vec{r}\,') - \left\langle \rho_m(\vec{r}\,')\right\rangle\right]\right\rangle$$

where $\rho_m(\vec{r}) \equiv \rho(\vec{r}_1,\cdots,\vec{r}_N\,|\vec{r})$ is the microscopic number density.

To show that

$$\sigma^2(\vec{r},\vec{r}\,') = \rho(\vec{r})\,\delta(\vec{r}-\vec{r}\,') + \rho(\vec{r})\,\rho(\vec{r}\,')\left[g(\vec{r},\vec{r}\,')-1\right]$$

use that the microscopic density is defined as

$$\rho_m(\vec{r}) = \sum_{j=1}^{N} \delta(\vec{r}-\vec{r}_j)$$

First of all, notice that, for identical particles

$$<\rho_m(\vec{r})> = \int d\vec{r}_1 \cdots \int d\vec{r}_N \left[\sum_{j=1}^{N} \delta(\vec{r}-\vec{r}_j)\right] P(\vec{r}_1,\cdots,\vec{r}_n) = N\,P_1(\vec{r}) = \rho(\vec{r})$$

with $\rho(\vec{r})$ the macroscopic density. Similarly, by definition

$$\begin{aligned}\sigma^2(\vec{r},\vec{r}\,') = \int d\vec{r}_1 \cdots \int d\vec{r}_N \ [&\sum_{i,j=1}^{N} \delta(\vec{r}\,'-\vec{r}_i)\,\delta(\vec{r}-\vec{r}_j) \\ &- <\rho_m(\vec{r})> \sum_{i=1}^{N} \delta(\vec{r}\,'-\vec{r}_i) - <\rho_m(\vec{r}\,')> \sum_{j=1}^{N} \delta(\vec{r}-\vec{r}_j) \\ &+ <\rho_m(\vec{r})><\rho_m(\vec{r}\,')>\,]\,P(\vec{r}_1,\cdots,\vec{r}_n)\end{aligned}$$

Using that

$$\int d\vec{r}_1 \cdots \int d\vec{r}_N \ \delta(\vec{r}\,'-\vec{r}_i)\,\delta(\vec{r}-\vec{r}_j)\,P(\vec{r}_1,\cdots,\vec{r}_n) = P_2(\vec{r},\vec{r}\,')$$

for $i \neq j$, while

$$\int d\vec{r}_1 \cdots \int d\vec{r}_N \ \delta(\vec{r}\,'-\vec{r}_i)\,\delta(\vec{r}-\vec{r}_j)\,P(\vec{r}_1,\cdots,\vec{r}_n) = P_1(\vec{r})\,\delta(\vec{r}-\vec{r}\,')$$

for $i = j$, and

$$\int d\vec{r}_1 \cdots \int d\vec{r}_N \ <\rho_m(\vec{r})> \sum_{i=1}^{N} \delta(\vec{r}\,'-\vec{r}_i) \ P(\vec{r}_1,\cdots,\vec{r}_n) = N <\rho_m(\vec{r})> P_1(\vec{r}\,')$$

and similarly for the other term, and using that the pdf for all position coordinates is normalized, it is found that

$$\begin{aligned}\sigma^2(\vec{r},\vec{r}\,') &= N(N-1)P_2(\vec{r},\vec{r}\,') + NP_1(\vec{r})\,\delta(\vec{r}-\vec{r}\,') \\ &\quad - N<\rho_m(\vec{r})>P_1(\vec{r}\,') - N<\rho_m(\vec{r}\,')>P_1(\vec{r}) + <\rho_m(\vec{r})><\rho_m(\vec{r}\,')>\end{aligned}$$

Substitution of the definition (1.52) in the book of the pair-correlation function immediately leads to

$$\sigma^2(\vec{r},\vec{r}\,') = \rho(\vec{r})\,\delta(\vec{r}-\vec{r}\,') + \rho(\vec{r})\,\rho(\vec{r}\,')\left[g(\vec{r},\vec{r}\,')-1\right]$$

provided that N is large.

Now define the phase function $N(\vec{r}_1,\cdots,\vec{r}_N)$ as

$$N(\vec{r}_1,\cdots,\vec{r}_N) = \int_V d\vec{r}\;\rho(\vec{r}_1,\cdots,\vec{r}_N\,|\vec{r}) \equiv \int_V d\vec{r}\;\rho_m(\vec{r})$$

which is the number of particles contained in the volume V. Suppose that the linear dimension of the volume V is much larger than the distance over which the pair-correlation function attains its limiting value of 1.

Integration of the defining equation for the standard deviation gives

$$\begin{aligned}\int_V d\vec{r}\int_V d\vec{r}\,'\,\sigma^2(\vec{r},\vec{r}\,') &= \left\langle \int_V d\vec{r}\left[\rho_m(\vec{r})-\langle\rho_m(\vec{r})\rangle\right]\int_V d\vec{r}\,'\left[\rho_m(\vec{r}\,')-\langle\rho_m(\vec{r}\,')\rangle\right]\right\rangle \\ &= \left\langle \left[N-<N>\right]^2\right\rangle\end{aligned}$$

where N is now understood to be the above defined phase function. Hence by integration of the above expression for the standard deviation

$$\left\langle\left(N-\langle N\rangle\right)^2\right\rangle = <N> + \left(\frac{<N>}{V}\right)^2\int_V d\vec{r}\int_V d\vec{r}\,'\left[g(\vec{r},\vec{r}\,')-1\right]$$

Since by assumption V is large as compared to the range over which the pair-correlation function tends to unity, and $g(\vec{r},\vec{r}\,') = g(|\vec{r}-\vec{r}\,'|) = g(R)$ for a homogeneous system, this leads to

$$\frac{\left\langle\left(N-\langle N\rangle\right)^2\right\rangle}{\langle N\rangle} = 1 + 4\pi\,\overline{\rho}\int dR\,R^2\,h(R)$$

where $h = g-1$ is so-called "total correlation function" and $\overline{\rho} =<N>/V$ is the average density. The total correlation function thus measures the amplitude of number fluctuations in large volumes.

Note that the relative standard deviation $\left\langle\left(N-\langle N\rangle\right)^2\right\rangle/\langle N\rangle^2$ tends to zero for large systems.

1.14 This exercise is related to Chapter 4, where **equations of motion** are discussed.

The pdf $P(\vec{r},t)$ for the position coordinate of a non-interacting Brownian particle at time t *satisfies* the following equation of motion (EOM),

$$\frac{\partial}{\partial t}P(\vec{r},t) = D_0\nabla^2 P(\vec{r},t)$$

The initial condition is $P(\vec{r},t=0)=\delta(\vec{r})$, which specifies that the particle is located at the origin at time $t=0$.

In this exercise we evaluate the collective dynamic structure factor, defined as

$$S_c(\vec{k},t-t_0) = \frac{1}{N}\left\langle \rho^*\left(\vec{X}(t_0)\middle|\vec{k}\right)\rho\left(\vec{X}(t)\middle|\vec{k}\right)\right\rangle$$

$$= \frac{1}{N}\sum_{i,j=1}^{N}\left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}_i(t_0)-\vec{r}_j(t)\right)\right]\right\rangle$$

The time-evolution operator for the particular case of non-interacting spheres under consideration here, according to the above equation of motion, is equal to $\hat{L} = D_0\nabla^2$.

For $i \neq j$, we have

$$\left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}_i(t=0)-\vec{r}_j(t)\right)\right]\right\rangle = \left\langle \exp\left[i\vec{k}\cdot\vec{r}_i(t=0)\right]\right\rangle\left\langle \exp\left[-i\vec{k}\cdot\vec{r}_j(t)\right]\right\rangle = 0$$

since

$$\left\langle \exp\left[-i\vec{k}\cdot\vec{r}_j(t)\right]\right\rangle = \frac{1}{V}\int_V d\vec{r}_j \exp\left[-i\vec{k}\cdot\vec{r}_j\right] \equiv \frac{(2\pi)^3}{V}\delta_V(\vec{k})$$

where the last line defines the function $\delta_V(\vec{k})$, which function, for large volumes, becomes equal to the delta function, which is zero for $\vec{k}\neq\vec{0}$. The structure factor for non-interacting particles thus reduces to

$$S_c(\vec{k},t) = \left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}_1(t=0)-\vec{r}_1(t)\right)\right]\right\rangle$$

For interacting particles, this will be defined later as the “self-dynamic structure factor”. For non-interacting particles the collective and self-dynamic structure factors are the same.

Written in terms of the Cartesian coordinates *x*, *y* and *z,* the time-evolution operator reads

$$\hat{L}\, e^{i\vec{k}\cdot\vec{r}} = D_0\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]e^{i\left(k_x x+k_y y+k_z z\right)}$$

It is readily verified that $\frac{\partial^2}{\partial x^2} e^{i\left(k_x x+k_y y+k_z z\right)} = -k_x{}^2 \, e^{i\left(k_x x+k_y y+k_z z\right)}$ and similarly for y and z. Hence

$$\hat{L}\exp\left(i\vec{k}\cdot\vec{r}\right) = \left(-D_0 k^2\right)\exp\left(i\vec{k}\cdot\vec{r}\right)$$

Repeating the operation n times leads to

$$\hat{L}^n \exp\left(i\vec{k}\cdot\vec{r}\right) = \left(-D_0 k^2\right)^n \exp\left(i\vec{k}\cdot\vec{r}\right)$$

so that

$$e^{\hat{L}t}\, e^{i\vec{k}\cdot\vec{r}} = \sum_{n=0}^{\infty}\frac{t^n}{n!}\hat{L}^n\, e^{i\vec{k}\cdot\vec{r}} = \left[\sum_{n=0}^{\infty}\frac{t^n}{n!}\left(-D_0 k^2\right)^n\right] e^{i\vec{k}\cdot\vec{r}} = e^{-D_0 k^2 t}\, e^{i\vec{k}\cdot\vec{r}}$$

Hence from eqn. (1.67) with $\vec{X} \equiv \vec{r}_1$, $f = e^{i\vec{k}\cdot\vec{r}_1}$ and $g = e^{-i\vec{k}\cdot\vec{r}_1}$, we find that

$$S_s = \frac{1}{V}\int d\vec{X}\, e^{-i\vec{k}\cdot\vec{r}_1}\, e^{-D_0 k^2 t}\, e^{i\vec{k}\cdot\vec{r}_1} = e^{-D_0 k^2 t}\int d\vec{X}\,\frac{1}{V} = e^{-D_0 k^2 t}$$

where it is used that the pdf for non-interacting particles is equal to *1/V.*

Here is a summary of the equations and results of this exercise:

$$\boxed{\begin{aligned}&\frac{\partial}{\partial t}P(\vec{r},t) = D_0\,\nabla^2 P(\vec{r},t)\\&\exp\left(\hat{L}t\right)\exp\left(i\vec{k}\cdot\vec{r}\right) = \exp\left(-D_0 k^2 t\right)\exp\left(i\vec{k}\cdot\vec{r}\right)\\&S_S(k,t) = \left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}_1(t=0)-\vec{r}_1(t)\right)\right]\right\rangle = \exp\left(-D_0 k^2 t\right)\end{aligned}}$$

Remember that all this refers to a very dilute suspension of spheres, where inter-colloidal interactions are neglected.

1.15 For non-interacting particles, the static structure factor is identically equal to 1 for $\vec{k} \neq 0$.

We will first show this from the defining equation

$$S(k) \equiv \frac{1}{N} \sum_{i,j=1}^{N} \left\langle \exp\left[i\vec{k} \cdot \left(\vec{r}_i - \vec{r}_j \right) \right] \right\rangle$$

of the structure factor. Since for $i \neq j$

$$\left\langle \exp\left[i\vec{k} \cdot \left(\vec{r}_i - \vec{r}_j \right) \right] \right\rangle = \left\langle \exp\left[i\vec{k} \cdot \vec{r}_i \right] \right\rangle \left\langle \exp\left[i\vec{k} \cdot \vec{r}_j \right] \right\rangle = 0$$

as already shown in exercise 1.14, only the terms with $i = j$ survive, which immediately leads to $S(k) = 1$ for $\vec{k} \neq 0$.

The same result is recovered from the middle expression in eqn. (1.72)

$$S(k) = 1 + \bar{\rho} \int d\vec{R}\, g(R)\, e^{i\vec{k} \cdot \vec{R}}$$

Since $$\int d\vec{R}\ e^{-i\vec{k} \cdot \vec{R}} = \left(2\pi\right)^3 \delta\left(\vec{k}\right) = 0$$

where $\delta(\vec{k})$ is the delta function, it follows that for $g(R) = 1$, again, $S(k) = 1$.

Note that the last equation in eqn.(1.72) is obtained from

$$\int d\vec{R}\, g(R)\, e^{i\vec{k} \cdot \vec{R}} = \int_0^{\infty} dR\, R^2 g(R) \left[\oint d\hat{R}\, e^{i\vec{k} \cdot R\hat{R}} \right]$$

where the last integral (between the square brackets) ranges over all orientations of $\vec{R}$ (that is, the spherical angular coordinates), and $\hat{R} = \vec{R} / R$ is the unit vector along $\vec{R}$, and

$$\oint d\hat{R}\, e^{i\vec{k} \cdot \vec{R}} = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, e^{ikR\cos\theta} = 2\pi \int_{-1}^{1} dx\ e^{ikRx} = 2\pi \frac{e^{ikR} - e^{-ikR}}{ikR} = 4\pi \frac{\sin\left(kR\right)}{kR}$$

Exercises Chapter 2:
BROWNIAN MOTION OF NON-INTERACTING PARTICLES

A dragonfly with a drag force in the oily solvent, taken at Juelich in Germany

2.1 Newton's equation of motion for a spherical Brownian particle is

$$\frac{d\vec{p}}{dt} = -\gamma \frac{\vec{p}}{M} + \vec{f}(t)$$

Let us first integrate once to obtain an expression for the momentum $\vec{p}(t)$ in terms of the fluctuating force $\vec{f}(t)$. In the first step, consider the equation of motion without the random force

$$\frac{d\vec{p}}{dt} = -\gamma \frac{\vec{p}}{M}$$

the solution of which is a single exponential

$$\vec{p}(t) = \vec{A}\, e^{-\frac{\gamma}{M}t}$$

where $\vec{A}$ is an integration constant. The method of "variation of constant" is based on making this constant a function of time (the "constant" is thus assumed to "vary with time"), in such a way that the full equation of motion is satisfied. Hence

$$\frac{d\vec{p}}{dt} = -\gamma \frac{\vec{p}}{M} + \frac{d\vec{A}(t)}{dt} e^{-\frac{\gamma}{M}t}$$

so that

$$\frac{d\vec{A}(t)}{dt} = \vec{f}(t)\, e^{+\frac{\gamma}{M}t}$$

and hence

$$\vec{A}(t) = \vec{A}(t=0) + \int_0^t dt'\, \vec{f}(t')\, e^{+\frac{\gamma}{M}t'}$$

This now immediately leads to

$$\boxed{\vec{p}(t) = \vec{p}(t=0)\, e^{-\frac{\gamma}{M}t} + \int_0^t dt'\vec{f}(t')\, e^{-\frac{\gamma}{M}(t-t')}}$$

Since $\vec{p}(t) = M\, d\vec{r}(t)/dt$, a second integration is necessary to obtain an explicit expression for the position coordinate $\vec{r}(t)$. Integration of the above expression for the momentum coordinate leads to an expression for the position coordinate involving the double integral

$$\int_0^t dt''\int_0^{t''} dt'\vec{f}(t')\, e^{-\frac{\gamma}{M}(t''-t')}$$

The integration range in the (t', t'') plane is indicated in Fig.2.7 by the dashed area. The vertical lines in the figure below indicate the new integration directions.

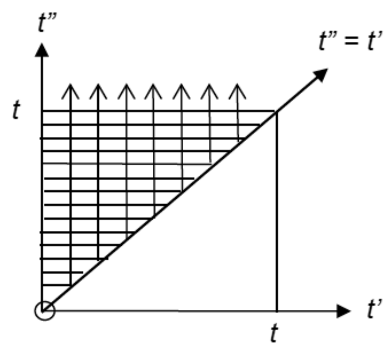


Fig. 2.7 The integration range in the (t’, t”) -plane

The integration ranges can be read-off the above figure.

It follows from this figure that an interchange of the order of integration leads to

$$\int_0^t dt'' \int_0^{t''} dt' \vec{f}(t')\, e^{-\frac{\gamma}{M}(t''-t')} = \int_0^t dt' \int_{t'}^{t''=t} dt'' \vec{f}(t')\, e^{-\frac{\gamma}{M}(t''-t')}$$
$$= \frac{M}{\gamma} \int_0^t dt' \vec{f}(t') \left[1 - e^{-\frac{\gamma}{M}(t-t')} \right]$$

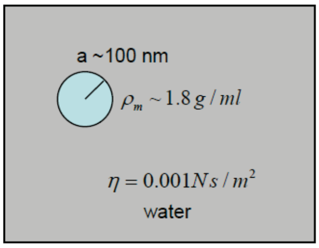
The final expression for the position coordinates in terms of the fluctuating force is therefore

$$\boxed{\vec{r}\left(t\right) = \vec{r}\left(t=0\right) + \frac{\vec{p}\left(t=0\right)}{\gamma}\left(1 - e^{-(\gamma/M)t}\right) + \frac{1}{\gamma}\int_0^t dt' f(t')\left(1 - e^{-(\gamma/M)(t-t')}\right)}$$

This is the expression that is used in the book to calculate the mean squared displacement.

2.3 A spherical Brownian particle with a radius of 100 *nm* and a mass density of 1.8 g/ml is immersed in water, with a viscosity of 0.001 Ns/m^2.

Use that the friction coefficient of a macroscopically large sphere is equal to $\gamma = 6\pi\eta_0 a$, to calculate the momentum relaxation time constant M/γ and its corresponding diffusive length scale l_D. Also calculate the time at which the mean squared displacement (MSD) is equal to the square of the radius of the Brownian sphere.



Plug into the numerical values of the given quantities

$$t \sim \frac{M}{\gamma} \sim \frac{(1.8-1.0)\left[g/ml\right] * \left(\frac{4\pi}{3}a^3\right)}{6\pi\eta_0 a} = \frac{0.8\left[g/ml\right] * \left(\frac{4\pi}{3}\right) * (100\ nm)^2}{6\pi * \left(1 * 10^{-3}\left[Ns/m^2\right]\right)} = 1.8\, ns$$

$$\frac{l_D}{a} \sim \frac{\sqrt{3Mk_BT}}{\gamma a} = \frac{\sqrt{3Mk_BT}}{6\pi\eta_0 a^2} = 1.1 \times 10^{-3}$$

The temperature is taken equal to 300 *K*, and the value of the Boltzmann constant is $1.38 \times 10^{-23}\ Nm/K$.

Also, the specific mass is corrected for that of water, which is 1.0 g/ml.

Since the mean squared displacement is given by

$$MSD = \left\langle \left|\vec{r}(t) - \vec{r}(t=0)\right|^2 \right\rangle = 6Dt = \frac{k_BT}{\pi\eta_0 a}t$$

so that the time at which the MSD is equal to the squared radius of the colloid is equal to

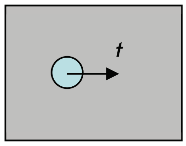
$$t = \frac{\pi\eta_0 a^3}{k_BT} = 76\, ms$$

This numerical example illustrates the time-scale separation that was mentioned in the main text of the book.

2. 4 Brownian motion in an external force field

A constant force field $\vec{F}$ is applied to a spherical Brownian particle, such as a gravitational force. The Langevin equation for this case reads

$$M\frac{d^2\vec{r}}{dt^2} = -\gamma\frac{d\vec{r}}{dt} + \vec{F} + \vec{f}$$



On the diffusive time scale, where $t \gg M/\gamma$, we can neglect the inertial force, so that

$$\frac{d\vec{r}}{dt} = \frac{1}{\gamma}\left[\vec{F} + \vec{f}\right]$$

The average, stationary velocity resulting from the force field $\vec{F}$ is equal to $<\vec{v}> = \vec{F}/\gamma$, thus the Langevin equation can be rewritten as

$$\frac{d}{dt}[\vec{p} - <\vec{p}>] = -\frac{\gamma}{M}[\vec{p} - <\vec{p}>] + \vec{f}$$

This is precisely the original Langevin equation in the absence of a field, where now the momentum is taken relative to the drift velocity. Since in this co-moving frame the equi-partition theorem holds, exactly the same analysis as without a field leads to

$$\lim_{t\to\infty}\left\langle(\vec{p}(t) - <\vec{p}>)(\vec{p}(t) - <\vec{p}>)\right\rangle = \hat{I}\frac{M}{\beta}$$

It follows that also in the present case with a constant force field

$$\left\langle \vec{f}(t)\right\rangle = 0$$
$$\left\langle \vec{f}(t)\vec{f}(t')\right\rangle = \hat{I}\frac{2\gamma}{\beta}\delta(t-t')$$

In order to find the probability density function (pdf) for the position coordinate, using Chandrasekhar's theorem, the above Langevin equation on the diffusive time scale is integrated once

$$\vec{r}(t) = \frac{1}{\gamma}\vec{F}\,t + \frac{1}{\gamma}\int_0^t dt'\,\vec{f}(t')$$

Comparing this with eqn.(2.29) we have the identification with the quantities defined in section 2.4 on Chandrasekhar's theorem

$$\boxed{\vec{X}(t) = \vec{r}(t) \qquad \vec{\Phi}(t) = \frac{1}{\gamma}\vec{F}\,t \qquad \Psi(t-t') = \frac{1}{\gamma} \qquad \vec{H} = \hat{I}\frac{2\gamma}{\beta}}$$

while the fluctuating force in eqn.(2.29) is $\vec{f}$ (note that our $\vec{F}$ is the constant external force, and should not be confused with the fluctuating force in eqn.(2.29) which is also denoted by a capital F). The matrix $\vec{M}$ in eqn. (2.33) is thus equal to

$$\vec{M} = \frac{2}{\gamma\beta}\hat{I}\, t$$

The determinant of this matrix is

$$\det(\vec{M}) = \left(\frac{2}{\gamma\beta}\, t\right)^3$$

and the inverse is

$$\vec{M}^{-1} = \frac{\gamma\beta}{2}\hat{I}\,\frac{1}{t}$$

According to Chandrasekhar's theorem (2.32)

$$P\left(\vec{X},t\right) = \frac{1}{\left(2\pi\right)^{3/2}\sqrt{\det \vec{M}}}\exp\left(-\frac{1}{2}\left(\vec{X}-\vec{\Phi}\left(t\right)\right)\bullet \vec{M}^{-1}\left(t\right)\bullet\left(\vec{X}-\vec{\Phi}\left(t\right)\right)\right)$$

it is thus found that

$$\boxed{P\left(\vec{r},t\right) = \frac{1}{\left(4\pi D_0 t\right)^{3/2}}\ \exp\left(-\frac{\left|\vec{r}-\vec{F}\,t/\gamma\right|^2}{4D_0 t}\right)}$$

where

$$D_0 = \frac{1}{\gamma\,\beta} = \frac{k_B T}{6\pi\eta_0 a}$$

is Einstein's diffusion coefficient. Note that we used here that $\vec{r}(t=0)=\vec{0}$.

2.5 Brownian motion in shear flow

We will calculate the mean position $\langle \vec{r}(t) \rangle$ and the mean squared displacement $\langle \vec{r}(t)\vec{r}(t) \rangle$ for a Brownian particle in a simple shear flow from the Langevin equation. The particle has an arbitrary initial position $\vec{r}_0$.

The local shear flow velocity is equal to

$$\vec{u}_0(\vec{r}) = \vec{\Gamma} \bullet \vec{r} \qquad\qquad \vec{\Gamma} = \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The Langevin equation reads

$$\frac{d\vec{p}}{dt} = -\gamma \left(\frac{\vec{p}}{M} - \vec{\Gamma} \bullet \vec{r} \right) + \vec{f}$$

Exactly as in exercise 2.4, it is shown that the strength of the fluctuating force is unaffected by the flow, so that, again (see also the discussion in section 2.7)

$$\langle \vec{f}(t) \rangle = 0$$

$$\langle \vec{f}(t)\vec{f}(t') \rangle = \hat{I} \frac{2\gamma}{\beta} \delta(t - t')$$

On the diffusive time scale, in the overdamped limit, the Langevin equation reduces to

$$\frac{d\vec{r}}{dt} = \vec{\Gamma} \bullet \vec{r} + \frac{1}{\gamma} \vec{f}$$

This differential equation is solved by the method of "variation of constants", which was already discussed in detail in exercise 2.1. Integration with the neglect of the fluctuating force Gives

$$\vec{r}(t) = \vec{r}_0 + \exp\{\vec{\Gamma} t\} \bullet \vec{A}$$

where $\vec{A}$ is an integration constant, and where the exponent of the matrix is defined as (see eqn.(2.58))

$$\exp\{\vec{\Gamma} t\} \equiv \sum_{n=0}^{\infty} \frac{1}{n!} \vec{\Gamma}^n \, t^n$$

From the definition of $\vec{\vec{\Gamma}}$ it is easily verified that $\vec{\vec{\Gamma}} \cdot \vec{\vec{\Gamma}} = \vec{\vec{0}}$, and hence $\vec{\vec{\Gamma}}^n = \vec{\vec{0}}$ for all $n > 1$. It thus follows that

$$\exp\{\vec{\vec{\Gamma}} t\} \equiv \hat{I} + \vec{\vec{\Gamma}}\, t$$

Hence

$$\vec{r}(t) = \vec{r}_0 + [\hat{I} + \vec{\vec{\Gamma}} t] \cdot \vec{A}$$

We now turn the vector $\vec{A}$ into a function of time, such that the full Langevin equation, including the fluctuating term, is satisfied. Substitution into the Langevin equation gives (use again that $\vec{\vec{\Gamma}} \cdot \vec{\vec{\Gamma}} = \vec{\vec{0}}$)

$$[\hat{I} + \vec{\vec{\Gamma}} t] \cdot \frac{d\vec{A}(t)}{dt} = \vec{\vec{\Gamma}} \cdot \vec{r}_0 + \frac{1}{\gamma} \vec{f}(t)$$

The inverse of the matrix $[\hat{I} + \vec{\vec{\Gamma}} t]$ is equal to $[\hat{I} - \vec{\vec{\Gamma}} t]$. It follows that

$$\frac{d\vec{A}(t)}{dt} = \vec{\vec{\Gamma}} \cdot \vec{r}_0 + \frac{1}{\gamma} \left[\hat{I} - \vec{\vec{\Gamma}}\, t \right] \cdot \vec{f}(t)$$

and hence

$$\vec{A}(t) = \vec{\vec{\Gamma}} \cdot \vec{r}_0\, t + \frac{1}{\gamma} \int_0^t dt' \left[\hat{I} - \vec{\vec{\Gamma}}\, t' \right] \cdot \vec{f}(t')$$

Finally, the position coordinate is found to be equal to

$$\vec{r}(t) = \vec{r}_0 + \vec{\vec{\Gamma}} \cdot \vec{r}_0\, t + \frac{1}{\gamma} \int_0^t dt'\, \vec{f}(t') + \frac{1}{\gamma} \int_0^t dt' (t - t')\, \vec{\vec{\Gamma}} \cdot \vec{f}(t')$$

The average position coordinate is thus equal to

$$< \vec{r} > (t) = \vec{r}_0 + \vec{\vec{\Gamma}} \cdot \vec{r}_0\, t$$

The interpretation of this result is that, on average, the particle is dragged along by the flow with a velocity equal to the local flow velocity

The mean squared displacement is equal to

$$< (\vec{r}(t) - \vec{r}_0)(\vec{r}(t) - \vec{r}_0) > = (\vec{\vec{\Gamma}} \cdot \vec{r}_0)(\vec{\vec{\Gamma}} \cdot \vec{r}_0)\, t^2 + \frac{1}{\gamma^2} \int_0^t dt' \int_0^t dt'' < \vec{f}(t')\, \vec{f}(t'') >$$

$$+ \frac{1}{\gamma^2} \int_0^t dt' \int_0^t dt''\ (t - t') \left[\vec{\vec{\Gamma}} \cdot < \vec{f}(t'')\, \vec{f}(t') > + < \vec{f}(t')\, \vec{f}(t'') > \cdot \vec{\vec{\Gamma}}^T \right]$$

$$+ \frac{1}{\gamma^2} \int_0^t dt' \int_0^t dt''\ (t - t')(t - t'')\ \vec{\vec{\Gamma}} \cdot < \vec{f}(t')\, \vec{f}(t'') > \cdot\, \vec{\vec{\Gamma}}^T$$

Using that the fluctuating force is delta-correlated it follows that the mean squared displacement $\ddot{W}_c(t)$ in the co-moving frame is equal to

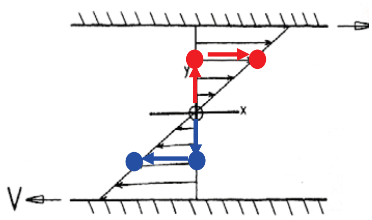
$$\ddot{W}_c(t) \equiv < (\vec{r}(t) - \vec{r}_0 - \vec{\Gamma}\bullet\vec{r}_0\, t)(\vec{r}(t) - \vec{r}_0 - \vec{\Gamma}\bullet\vec{r}\ t) >$$
$$= 2\hat{I}D_0 t + 2\hat{E}D_0 t^2 + \frac{2}{3}\ddot{U}D_0 t^3$$

where $D_0 = 1/\gamma\beta$ is the Einstein diffusion coefficient, and

$$\hat{E} = \frac{1}{2}\left[\vec{\Gamma} + \vec{\Gamma}^T\right] \qquad \ddot{U} = \vec{\Gamma}\bullet\vec{\Gamma}^T = \vec{\Gamma}^T\bullet\vec{\Gamma}$$

In matrix notation this reads

$$\ddot{W}_c(t) = \ddot{W}_0(t) + 2D_0 t \begin{pmatrix} \frac{1}{3}\dot{\gamma}^2 t^2 & \frac{1}{2}\dot{\gamma}t & 0 \\ \frac{1}{2}\dot{\gamma}t & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



with $\ddot{W}_0(t) = 2\hat{I}D_0 t$ the mean squared displacement in the absence of flow.

The effect of flow is measured by the difference $\Delta\ddot{W}(t) = \ddot{W}_c(t) - \ddot{W}_0(t)$, which is the matrix that is written explicitly in the above expression. All components of $\Delta\ddot{W}(t)$ where one of the indices refers to the z-direction are zero. This is the vorticity direction, which is both perpendicular to the flow and gradient direction. Diffusion in the vorticity direction is thus unaffected, which is intuitively expected. Also the yy-components of $\ddot{W}(t)$ is unaffected by flow.

The probability to move upwards in the gradient direction is equal to that for a displacement downwards, giving on average a zero net effect. That the xy- and yx-components are affected by flow can be understood as follows.

As depicted in the figure, if the particle moves downward, to lower values of its position y in the gradient direction, the flow will induce an additional velocity to the left. When the particle moves upwards, it attains an equal change in velocity in the opposite direction.

The product of these two displacements is equal, so that there is a non-zero contribution. That the xx-component of $\Delta\ddot{W}(t)$ is non-zero is easily understood: when the particle happens to be displaced in the y-direction, the displacement in the x-direction is very much enhanced since the particle is taken along with the flow, precisely as was already depicted in the figure.

2.6 In this exercise we consider a Brownian particle when one can occupy only discrete positions $n \in \{\cdots,-3,-2,-1,0,1,2,3,\cdots\}$ that are indexed by integers.

Suppose that the probability per unit time for a single step to the left or the right side is equal to α . Let $P(n,t)$ denote the conditional pdf for the position n of the Brownian particle, given that at time $t=0$ the position was equal to n_0 .

For simplicity of notation, we shall take $n_0 = 0$, and refrain from the explicit notation of the condition in the argument of the pdf. The equation of motion (EOM) is

$$\frac{\partial P(n,t))}{\partial t} = \alpha\left\{ P(n+1,t) + P(n-1,t) - 2P(n,t) \right\}$$

The interpretation of the various terms on the right is as follows.

If a particle resides at position $n+1$, the probability that it jumps per unit time to the neighboring position n is α, multiplied by the probability $P(n+1,t)$ that the particle is at position $n+1$. The product $\alpha P(n+1,t)$ is thus the rate of increase of $P(n,t)$ due to jumps from $n+1$ to n.

This explains the first term on the right hand side, and similarly the second terms account for jumps from $n-1$ to n . The last term of the right hand side accounts for jumps away from position n , to the left or right, giving rise to the factor 2.

To calculate the average displacement $<n>$, both sides of the EOM are multiplied by n , and then a summation over all positions is performed.

The left hand side gives,

$$\frac{d}{dt}\sum_{n=-\infty} n\,P(n,t) = \frac{d}{dt} < n >$$

The first term on the right hand side gives,

$$\sum_{n=-\infty}^{\infty} n\,P(n+1,t) = \sum_{m=-\infty}^{\infty} (m-1)\,P(m,t) = < n > -1$$

and similarly for the remaining terms. This leads to

$$\frac{d}{dt} < n > = \alpha\left\{ < n > + < n > -2 < n > \right\} = 0$$

Since $<n> = 0$ at time $t=0$, time integration gives

$$< n > = 0$$

To calculate the mean squared displacement, multiply the EOM by n^2 and sum over all n . The first term on the right hand side of the EOM, as an example, is equal to

$$\sum_{n=-\infty}^{\infty} n^2 \, P\left(n+1,t\right) = \sum_{m=-\infty}^{\infty} (m-1)^2 \, P\left(m,t\right)$$
$$= \sum_{m=-\infty}^{\infty} (m^2 - 2m + 1) \, P\left(m,t\right) = < n^2 > -2 < n > +1$$

The following EOM for the mean squared displacement is found

$$\frac{d}{d\,t} < n^2 > = \alpha \left\{ (< n^2 > -2 < n > +1) + (< n^2 > +2 < n > +1) - 2 < n^2 > \right\} = 2\,\alpha$$

Integration, using that the mean squared displacement is zero at time zero finally gives

$$< n^2 > = 2\,\alpha t$$

The mean squared displacement is again found to be a linear function of time.

Comparing this with eqn. (2.21), the diffusion coefficient D is thus equal to α .

Note that the factor of “2” in the above equation and that in eqn. (2.21) both relate to diffusion in a single dimension.

2.7 Translational velocity of a rod

If the orientation $\hat{u}$ of the rod is not along or perpendicular to the external force $\vec{F}$, the velocity that the rods attains is not co-linear with the external force, since the friction coefficients $\gamma_{\parallel}$ and $\gamma_{\perp}$ for parallel and perpendicular motion are not equal.

For stationary motion, we have

$$\vec{F} = \vec{\Gamma}_f \bullet \vec{v} \qquad \vec{\Gamma}_f = \gamma_{\parallel}\, \hat{u}\hat{u} + \gamma_{\perp}\left(\hat{I} - \hat{u}\hat{u}\right)$$

For long and thin rods

$$\gamma_{\parallel} = \frac{2\pi\eta_0 L}{\ln\left(L/D\right)} \qquad \gamma_{\perp} = 2\gamma_{\parallel},$$

Inverting the friction tensor gives the velocity in terms of the force

$$\vec{v} = \vec{\Gamma}_f^{-1} \bullet \vec{F} \qquad \vec{\Gamma}_f^{-1} = \frac{1}{\gamma_{\parallel}}\hat{u}\hat{u} + \frac{1}{\gamma_{\perp}}\left(\hat{I} - \hat{u}\hat{u}\right)$$

The cosine of the angle Θ between the external force and the velocity is

$$\cos\{\Theta\} = \hat{F} \cdot \hat{v}$$

where $\hat{F} = \vec{F}/F$ and $\hat{v} = \vec{v}/v$ are the unit vectors along the force and velocity, respectively. Hence, from the above expression for the velocity in terms of the force

$$\vec{v} \bullet \vec{F} = \left(\frac{1}{\gamma_{\parallel}} - \frac{1}{\gamma_{\perp}}\right)(\hat{u} \bullet \vec{F})^2 + \frac{1}{\gamma_{\perp}}F^2$$

$$v = \left[\left(\frac{1}{\gamma_{\parallel}^2} - \frac{1}{\gamma_{\perp}^2}\right)(\hat{u} \bullet \vec{F})^2 + \frac{1}{\gamma_{\perp}^2}F^2\right]^{1/2}$$

Hence

$$\cos\{\Theta\} = \frac{\left(\frac{1}{\gamma_{\parallel}} - \frac{1}{\gamma_{\perp}}\right)(\hat{u} \bullet \hat{F})^2 + \frac{1}{\gamma_{\perp}}}{\left[\left(\frac{1}{\gamma_{\parallel}^2} - \frac{1}{\gamma_{\perp}^2}\right)(\hat{u} \bullet \hat{F})^2 + \frac{1}{\gamma_{\perp}^2}\right]^{1/2}}$$

This result is valid also for short rods. In case of very long and thin rods, where $\gamma_{\perp} = 2\gamma_{\parallel}$, the above result reduces to

$$\cos\{\Theta\} = \frac{1 + (\hat{u} \bullet \hat{F})^2}{\left[1 + 3(\hat{u} \bullet \hat{F})^2\right]^{1/2}}$$

When the force is parallel to the orientation of the rod, $\hat{u} \bullet \hat{F} = 1$, or when they are perpendicular, $\hat{u} \bullet \hat{F} = 0$, both equations give and angle equal to zero. That is, for these two orientations the rod's velocity is parallel to the external force (see also the right figure below).

For other orientations of the rod, relative to the external force, the angle is non-zero.

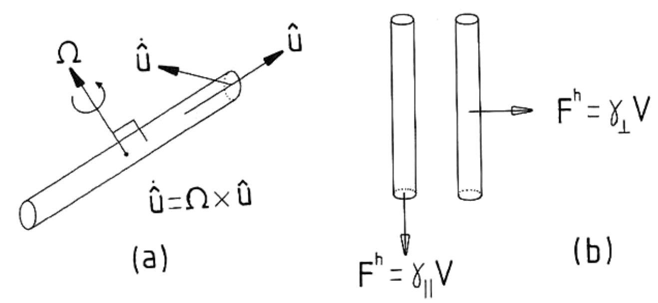


Fig. 2.5: (a) Rotation and (b) translation of a cylindrically symmetric rod.

2.8 The diffusive angular time scale

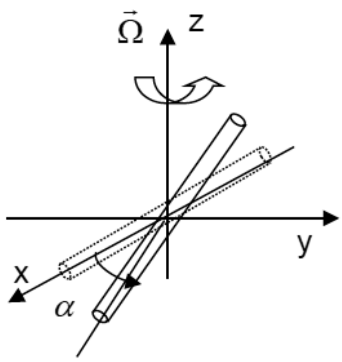
The thermally averaged Langevin equation (2.129) reads,

$$\frac{1}{12} ML^2 \frac{d\vec{\Omega}}{dt} = -\gamma_r \vec{\Omega}$$

where $\vec{\Omega}$ is the rotational velocity. The solution of this differential equation is

$$\vec{\Omega} = \vec{\Omega}_0 \exp\{-t/\tau\} \qquad \tau = \frac{1}{12}\frac{ML^2}{\gamma_r}$$

Consider a rod that at time zero is aligned along the x-direction and the angular velocity $\vec{\Omega}_0$ at time zero is along the z-axis, as shown in the figure below.



The direction of the angular velocity remains along the z-direction, and only its magnitude decreases with time (as can be seen from the above equation), due to friction with the solvent.

The orientation of the rod is therefore always within the xy-plane. Hence we can write

$$\hat{u}_x = \cos(\alpha) \qquad \hat{u}_y = \sin(\alpha)$$

with α the angle of the orientation with the y-axis (see the figure). Hence

$$\vec{\Omega} = \hat{u} \times \frac{d\hat{u}}{dt} = \hat{e}_z \left[\hat{u}_x \frac{d\hat{u}_y}{dt} - \hat{u}_y \frac{d\hat{u}_x}{dt} \right] = \hat{e}_z \frac{d\alpha(t)}{dt}$$

where $\hat{e}_z$ is unit vector along the z-axis. Thus

$$\frac{d\alpha(t)}{dt} = \Omega_0 \exp\{-t/\tau\}$$

Integration thus leads to

$$\alpha(t) = \tau \Omega_0 \left[1 - \exp\{-t/\tau\}\right] \approx \tau \Omega_0 \qquad t \gg \tau$$

The angular displacement during relaxation of the angular momentum is thus equal to

$$\Delta\alpha = \tau\,\Omega_0 \approx \frac{ML^2}{12\gamma_r} 6\sqrt{\frac{k_B T}{ML^2}} = \frac{\sqrt{k_B T M L^2}}{2\gamma_r}$$

where we used that a typical value for Ω_0, according to eqn.(2.118) is equal to

$$\Omega_0 \approx \sqrt{< \Omega^2 >} = 6\sqrt{\frac{k_B T}{ML^2}}$$

Typical values are $M \approx 10^{-18}\,kg$, $L \approx 10^{-6}\,m$ and $\gamma_r \approx 10^{-22}\,Nms$, from which it is found that

$$\Delta\alpha \approx 3\times 10^{-4}\,radians \approx 0.02^0$$

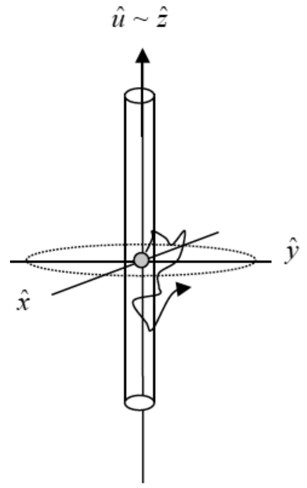
The angular displacement during relaxation of the angular momentum is thus much smaller than a degree.

2.9 For a fixed orientation of the rod along the z-direction, the Langevin equations (2.86,87), read, on the diffusive time scale where $d\vec{p}\,/\,dt$ can be set to zero

$$\overleftrightarrow{\Gamma}_f \bullet \frac{d\vec{r}(t)}{dt} = \vec{f}(t) = \vec{f}_\perp(t) + \vec{f}_\parallel(t)$$

The friction tensor is equal to (see eqn.(2.91))

$$\overleftrightarrow{\Gamma}_f = \gamma_\parallel \hat{u}\hat{u} + \gamma_\perp [\hat{I} - \hat{u}\hat{u}]$$



the inverse of which is,

$$\overleftrightarrow{\Gamma}_f^{-1} = \frac{1}{\gamma_\parallel}\hat{u}\hat{u} + \frac{1}{\gamma_\perp}[\hat{I} - \hat{u}\hat{u}]$$

so that the above over-damped Langevin equation reads

$$\frac{d\vec{r}(t)}{dt} = \frac{1}{\gamma_\perp}\vec{f}_\perp(t) + \frac{1}{\gamma_\parallel}\vec{f}_\parallel(t)$$

where it is used that

$$\hat{u}\hat{u} \bullet \vec{f}_\perp = \vec{0} \qquad [I - \hat{u}\hat{u}] \bullet \vec{f}_\perp = \vec{f}_\perp$$
$$\hat{u}\hat{u} \bullet \vec{f}_\parallel = \vec{f}_\parallel \qquad [I - \hat{u}\hat{u}] \bullet \vec{f}_\parallel = \vec{0}$$

Integration thus gives

$$\vec{r}(t) = \vec{r}(0) + \int_0^t dt' \left[\frac{1}{\gamma_\perp}\vec{f}_\perp(t') + \frac{1}{\gamma_\parallel}\vec{f}_\parallel(t') \right]$$

For the x-component it is thus found that

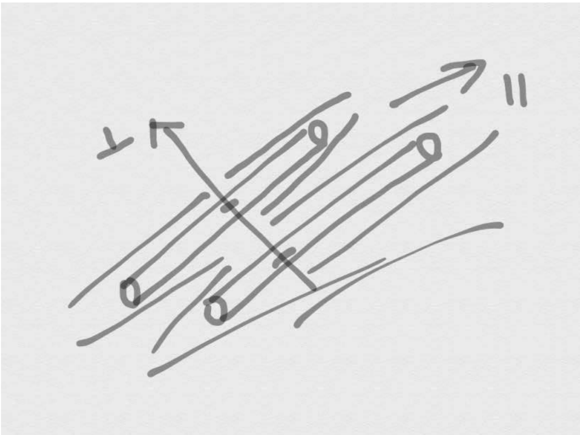
$$x(t) - x(0) = \frac{1}{\gamma_\perp} \int_0^t dt' \; f_{x,\perp}(t')$$

with $f_{x,\perp}(t')$ the x-component of the perpendicular fluctuating force.

Hence, from eqns. (2.107, 112)

$$< (x(t) - x(0))^2 > = \frac{1}{\gamma_\perp^2} \int_0^t dt' \int_0^t dt'' < f_{x,\perp}(t') \, f_{x,\perp}(t'') > = \frac{2\gamma_\perp k_B T \, t}{\gamma_\perp^2} = 2D_\perp t$$

Note that we used in eqn. (2.107), that we only consider here the x-component of the force, giving rise to the factor 2 instead of 4 in the fluctuation strength. The two other mean squared displacements follow similarly.



Exercises Chapter 3: LIGHT SCATTERING

3.3 In the evaluation of the scattered intensity, the following integral is encountered

$$I(k) \equiv \int d\vec{k}\,\frac{\exp\left(i\vec{k}\cdot(\vec{r}-\vec{r}\,")\right)}{k^2-\left(k_0+i\alpha\right)^2}$$

In order to perform the spherical integration, we rewrite this as

$$I(k) = \int_0^\infty dk k^2 \frac{1}{k^2-\left(k_0+i\alpha\right)^2}\oint d\hat{k}\exp\left(ik\hat{k}\cdot(\vec{r}-\vec{r}\,")\right)$$

where $\vec{k}=k\,\hat{k}$ with $\hat{k}$ the unit vector along $\vec{k}$. The last integral is with respect to the orientation of the wave vector, that is, the two spherical angles. Since the integral is independent of the direction of the wave vector, the angular integral can be written as

$$\begin{aligned}
\oint d\hat{k}\exp\left(ik\hat{k}\cdot(\vec{r}-\vec{r}\,")\right) &= \int_0^{2\pi} d\varphi\int_0^{\pi} d\theta\,\sin\{\theta\}\exp\left(ik\cos\{\theta\}\left|\vec{r}-\vec{r}\,"\right|\right) \\
&= 2\pi\int_{-1}^{1} dx\,\exp\left(ikx\left|\vec{r}-\vec{r}\,"\right|\right) \\
&= 2\pi\frac{\exp\left(ik\left|\vec{r}-\vec{r}\,"\right|\right)-\exp\left(-ik\left|\vec{r}-\vec{r}\,"\right|\right)}{ik\left|\vec{r}-\vec{r}\,"\right|} \\
&= 4\pi\frac{\sin\{k\left|\vec{r}-\vec{r}\,"\right|\}}{k\left|\vec{r}-\vec{r}\,"\right|}
\end{aligned}$$

Hence

$$I(k) = 4\pi\int_0^\infty dk\,\frac{k^2}{k^2-(k_0+i\alpha)^2}\,\frac{\sin\{k\left|\vec{r}-\vec{r}\,"\right|\}}{k\left|\vec{r}-\vec{r}\,"\right|}$$

Since the integrand is an even function of *k*, we can replace the integral from zero to infinity by half of the integral from minus infinity to plus infinity. Re-expressing the sinus as a sum of exponential, we thus arrive at

$$I(k) = \frac{\pi}{i}\int_{-\infty}^{\infty} dk\,\frac{k}{k^2-(k_0+i\alpha)^2}\left[\frac{\exp\{i\,k\left|\vec{r}-\vec{r}\,"\right|\}}{\left|\vec{r}-\vec{r}\,"\right|}-\frac{\exp\{-i\,k\left|\vec{r}-\vec{r}\,"\right|\}}{\left|\vec{r}-\vec{r}\,"\right|}\right]$$

Consider the first integral, which can be evaluated by means of the residue theorem by closing in the upper part of complex half plane, as depicted in the left of figure 3.3.

There is just a single first order pole at $k=k_0+i\alpha$.

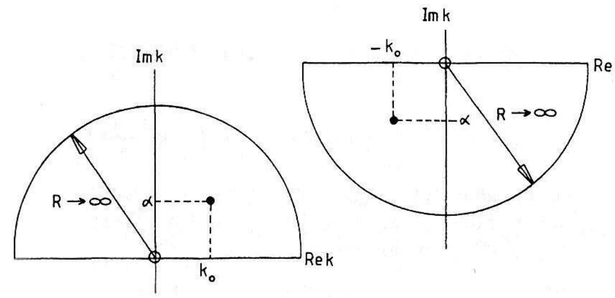


Fig. 3.3 The integration contours for the evaluation of the k-integral in eqn. (3.36).

According to the residue theorem we thus arrive (for $\alpha \to 0$) at

$$\frac{\pi}{i}\int_{-\infty}^{\infty} dk \frac{k^2}{k^2-(k_0+i\alpha)^2}\frac{\exp\{i\,k|\vec{r}-\vec{r}\,''|\}}{k|\vec{r}-\vec{r}\,''|} = \frac{\pi}{i}2\pi i\frac{k_0+i\alpha}{2(k_0+i\alpha)}\frac{\exp\{i(k_0+i\alpha)|\vec{r}-\vec{r}\,''|\}}{|\vec{r}-\vec{r}\,''|}$$
$$= \pi^2\frac{\exp\{i\,k_0|\vec{r}-\vec{r}\,''|\}}{|\vec{r}-\vec{r}\,''|}$$

The second integral is evaluated similarly, and turns out to be equal to the first integral. Hence

$$I(k) = 2\pi^2\frac{\exp\left\{ ik_0|\vec{r}-\vec{r}\,''|\right\}}{|\vec{r}-\vec{r}\,''|}$$

Now use that (with $R = |\vec{r}-\vec{r}\,''|$)

$$\nabla\left(\frac{\exp\{ik_0|\vec{r}-\vec{r}\,''|}{|\vec{r}-\vec{r}\,''|}\right) = \frac{\vec{r}-\vec{r}\,''}{|\vec{r}-\vec{r}\,''|}\frac{d}{dR}\frac{\exp\{ik_0R\}}{R}$$
$$= \frac{\vec{r}-\vec{r}\,''}{|\vec{r}-\vec{r}\,''|}\left[ik_0|\vec{r}-\vec{r}\,''|-1\right]\exp\left\{ ik_0|\vec{r}-\vec{r}\,''|\right\}$$

A second differentiation gives

$$\nabla\nabla\left(\frac{\exp\{ik_0|\vec{r}-\vec{r}\,''|}{|\vec{r}-\vec{r}\,''|}\right) = \frac{\hat{I}}{|\vec{r}-\vec{r}\,''|^3}\left[ik_0|\vec{r}-\vec{r}\,''|-1\right]\exp\left\{ ik_0|\vec{r}-\vec{r}\,''|\right\}$$
$$+\frac{(\vec{r}-\vec{r}\,'')(\vec{r}-\vec{r}\,'')}{|\vec{r}-\vec{r}\,''|}\frac{d}{dR}\left(\left[\frac{ik_0R-1}{R^3}\right]\exp\{ik_0R\}\right)$$

Performing the differentiation with respect to *R* and adding the various contributions leads to eqn. (3.37).

3.4 The scattered electric field strength is calculated for a fixed configuration of Brownian particles (see Fig.3.1), which is a valid procedure when the phase change of the scattered light due to Brownian motion is small during the time that light needs to propagate through the cuvette. The time required for light to travel over a distance of the typical size of 1 cm of the cuvette, with water as the solvent (for which the refractive index is *1.3*), is equal to

$$t = 1[cm]/(300.000/1.3)[km/s] \approx 0.04[ns]$$

A typical diffusion coefficient for a colloid is $D \approx 10^{-12}\,[m/s^2]$.

The displacement of a single colloidal particle during *0.04* [*ns*] is therefore

$$l \approx \sqrt{6D\,t} \approx 0.015\,nm$$

A appropriate upper limit for the relative displacement of two colloids is therefore *2l=0.03 nm.* A typical value for the scattering vector is $4\pi\,(n=1.3)/\lambda_0$, where $\lambda_0 = 600\,nm$ is the wavelength of the light in vacuum.

The change in phase shift is therefore

$$\Delta\varphi \approx 0.03[nm]4\pi \times 1.3/600[nm] \approx 8\times 10^{-4}\,[rad] \approx 0.05^0$$

This phase shift is very small, and can be therefore neglected. This validates the calculation of the phases as if the colloidal-particle configuration does not change during the time needed for light to propagate through the system.

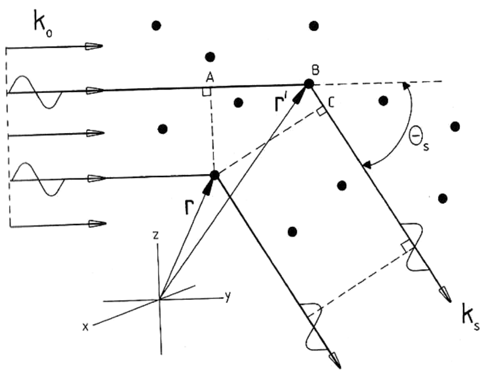


Fig. 3.1: A schematic representation of the scattering of light by an assembly of point-like particles. Each of the Brownian particles can comprise many of the point-like scatterers.

3.6 Expressing the static structure factor in terms of the total pair-correlation function, the integral

$$\overline{\rho}\int_{V_s} d\vec{r}\; g(\vec{r})\exp\{i\vec{k}\bullet\vec{r}\}$$

with V_S the scattering volume, is replaced by the integral

$$\overline{\rho}\int_{V_s} d\vec{r}\,[g(\vec{r})-1]\exp\{i\vec{k}\bullet\vec{r}\}$$

for non-zero wave vectors. It is thus assumed that

$$\overline{\rho}\int_{V_S} d\vec{r}\,\exp\{i\vec{k}\bullet\vec{r}\} \ll 1$$

We calculate the integral for two scattering geometries: (i) the scattering volume is a rectangular box, where the incident intensity within the box is constant, and is zero outside the box, and (ii) the more realistic case, where the incident intensity is Gaussian.

(i) The integral for the rectangular box is equal to

$$\overline{\rho}\left[\int_{-l/2}^{l/2} dx\exp\{ikx\}\right]^3 = \overline{\rho}\left.\frac{\exp\{ikx\}}{ik}\right|_{-l/2}^{l/2} = \overline{\rho}\,l^3\left[\frac{\sin\{kl/2\}}{kl/2}\right]^3$$

where l is the linear dimension of the box and $k \sim 2*10^7 m^{-1}$ is a typical value of the wave vector. Substitution of the typical values $l = 0.5\,mm$ and $\overline{\rho} \sim 10^{19}\,m^{-3}$ shows that this integral is quite large: $\sim 10^{22}$. The above claimed smallness of the integral is thus completely false for the rectangular scattering volume.

(ii) In this case, the incident intensity reads $I(r) = I_0\exp\{-(r/l)^2\}$, where r is the radial distance from the center of the scattering volume, and I_0 measures the overall (constant) intensity of the incident light. The integral is now equal to (see section 1.3.4 in the book)

$$\overline{\rho}\int d\vec{r}\,\frac{I(r)}{I_0}\exp\{i\vec{k}\bullet\vec{r}\} = (2\pi)^3\,\overline{\rho}\,l^3\exp\left\{-\frac{k^2l^2}{2}\right\}$$

We now find that the integral is extremely small.

The conclusion is that an unrealistically sharp edge of the scattering volume gives rise to very large Fourier components: the actual scattering pattern now contains very intensive scattering rings. For the realistic case of smooth edges, the above calculation justifies the neglect of the integral.

3.7 Small size polydispersity and static light scattering

(a) The polydisperse form factor is defined as the intensity normalized to unity at zero wavevector,

$$P^{pol}(k) \equiv R^{pol}(k) / R^{pol}(k=0)$$

where

$$R^{pol}(k) = \int_0^\infty da\, P_0(a)\, R(k,a)$$

is the measured "polydisperse" Rayleigh ratio for a dilute suspension. Here a is the colloidal radius and P_0 is the size-distribution function.

For optically homogeneous particles,

$$R(k,a) = K^* a^6\, P(k) = K^* a^6 \left[3 \frac{ka\cos(ka) - \sin(ka)}{(ka)^3} \right]^2$$

where

$$K^* = \frac{k_0^{\,4}}{9} \bar{\rho} \left| \frac{\bar{\varepsilon}_p - \varepsilon_f}{\varepsilon_f} \right|^2 = \frac{k_0^{\,4}}{9} \bar{\rho}\, C$$

is the optical contrast.

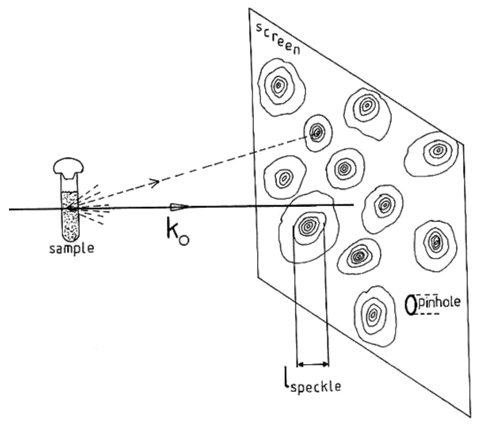


Fig. 3.8: The instantaneous speckle pattern of the scattered light. The circular hole in the screen is the detector pinhole.

In order to expand around the average radius $a = \overline{a}$, we use,

$$a^6 \, P\left(k,a\right) \equiv f(a) = f(\overline{a}) + \frac{df(\overline{a})}{d\overline{a}}\left(a-\overline{a}\right) + \frac{1}{2}\frac{d^2 f(\overline{a})}{d\overline{a}^2}\left(a-\overline{a}\right)^2$$

$$\frac{d\left(\overline{a}^6 P\left(k,a\right)\right)}{d\overline{a}} = 6\,\overline{a}^5 \, P\left(k,\overline{a}\right) + \overline{a}^6 \, \frac{dP(k,\overline{a})}{d\overline{a}}$$

$$\frac{d^2\left(\overline{a}^6 P\left(k,a\right)\right)}{d\overline{a}^2} = 30\,\overline{a}^4 \, P\left(k,\overline{a}\right) + 12\,\overline{a}^5 \, \frac{dP(k,\overline{a})}{d\overline{a}} + \overline{a}^6 \, \frac{d^2 P(k,\overline{a})}{d\overline{a}^2}$$

where $P(k,\overline{a})$ is the form factor of a sphere with the average radius $\overline{a}$

$$\overline{a} = \int_0^\infty da \, P_0(a) \, a$$

The standard deviation in size is defined as

$$\sigma^2 = \int_0^\infty da \, P_0(a) \left(a - \overline{a}\right)^2$$

A Taylor expansion also gives

$$a^6 \approx \overline{a}^6 + 6\,\overline{a}^5\left(a-\overline{a}\right) + 15\,\overline{a}^4\left(a-\overline{a}\right)^2$$

Using the above expansions we have

$$P^{pol}(k) = \frac{\int_0^\infty da \, P_0(a) \, a^6 P(k,a)}{\int_0^\infty da \, P_0(a) \, a^6},$$

$$\approx \frac{\int_0^\infty da \, P_0(a)\left[\overline{a}^6 P(k,\overline{a}) + \frac{1}{2}\left(a-\overline{a}\right)^2\left[30\,\overline{a}^4 \, P\left(k,\overline{a}\right) + 12\,\overline{a}^5 \, \frac{dP(k,\overline{a})}{d\overline{a}} + \overline{a}^6 \, \frac{d^2 P(k,\overline{a})}{d\overline{a}^2}\right]\right]}{\int_0^\infty da \, P_0(a)\left[\overline{a}^6 + 15\,\overline{a}^4\left(a-\underline{a}\right)^2\right]}$$

Further expansion in terms of the small quantity $\sigma / \overline{a}$ leads to

$$P^{pol}(k) \approx \frac{1}{\overline{a}^6}\left[\overline{a}^6 P(k,\overline{a}) + \frac{1}{2}\sigma^2\left[30\,\overline{a}^4\, P\left(k,\overline{a}\right) + 12\,\overline{a}^5\,\frac{dP(k,\overline{a})}{d\overline{a}} + \overline{a}^6\,\frac{d^2P(k,\overline{a})}{d\overline{a}^2}\right]\right]\left(1 - 15\frac{\sigma^2}{\overline{a}^2}\right)$$

$$= \frac{1}{\overline{a}^6}\left\{\overline{a}^6 P(k,\overline{a}) + \frac{1}{2}\sigma^2\left[30\,\overline{a}^4\, P\left(k,\overline{a}\right) + 12\,\overline{a}^5\,\frac{dP(k,\overline{a})}{d\overline{a}} + \overline{a}^6\,\frac{d^2P(k,\overline{a})}{d\overline{a}^2}\right] - 15\frac{\sigma^2}{\overline{a}^2}\overline{a}^6 P(k,\overline{a})\right\}$$

$$= P(k,\overline{a}) + \frac{1}{2}\frac{\sigma^2}{\overline{a}^2}\left\{12\,\overline{a}\,\frac{dP(k,\overline{a})}{d\overline{a}} + \overline{a}^2\,\frac{d^2P(k,\overline{a})}{d\overline{a}^2}\right\}$$

$$\approx P(k,\overline{a}) + \frac{\sigma^2}{\overline{a}^2}\left\{\frac{1}{2\overline{a}^4}\frac{d^2\left(\overline{a}^6 P(k,\overline{a})\right)}{d\overline{a}^2} - 15P(k,\overline{a})\right\}$$

This polydisperse form factor is plotted in Fig.3.11 as a function of ka_0 for various relative standard deviations $\sigma/\overline{a}$. As a result of polydispersity, the minima in the scattering curves become less pronounced.

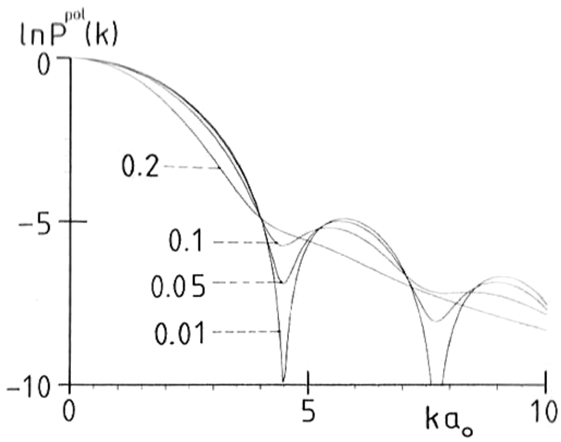


Fig. 3.11: The logarithm of the polydisperse form factor versus ka_0

$$P^{pol}(k) \equiv R^{pol}(k)/R^{pol}(k=0)$$

for various values of the relative standard deviation of $\sigma/\overline{a}$, as indicated by the numbers attached to the different curves

(b) For small wavevectors, i.e. $ka \ll 1$, the polydisperse radius a^{pol} is defined as

$$P^{pol}(k) \approx \exp\left(-\frac{1}{5}k^2\left(a^{pol}\right)^2\right) \approx 1-\frac{1}{5}k^2\left(a^{pol}\right)^2$$

which is the radius that is experimentally obtained, assuming monodisperse optically homogeneous Brownian particles. In the following we will show that to leading order in the polydispersity

$$\boxed{a^{pol} = \bar{a}\sqrt{1+13\left(\frac{\sigma}{\bar{a}}\right)^2} \approx \bar{a}\left[1+\frac{13}{2}\left(\frac{\sigma}{\bar{a}}\right)^2\right]}$$

By using the result for P^{pol} of (a), and

$$\bar{P}(k,\bar{a}) = 1-\frac{1}{5}k^2\bar{a}^2$$

it is found that

$$\begin{aligned}
P^{pol}(k) &\approx 1-\frac{1}{5}k^2\left(a^{pol}\right)^2 \\
&= 1-\frac{1}{5}k^2\bar{a}^2+\frac{1}{2}\frac{\sigma^2}{\bar{a}^2}\left\{12\,\bar{a}\left(-\frac{1}{5}k^2\left(2\,\bar{a}\right)\right)+\bar{a}^2\left(-\frac{1}{5}k^2\left(2\right)\right)\right\} \\
&= 1-\frac{1}{5}k^2\bar{a}^2+\frac{1}{2}\frac{\sigma^2}{\bar{a}^2}\left\{-\frac{1}{5}k^2\left(24\,\bar{a}^2\right)-\frac{1}{5}k^2\left(2\,\bar{a}^2\right)\right\} \\
&= 1-\frac{1}{5}k^2\bar{a}^2+\frac{1}{2}\frac{\sigma^2}{\bar{a}^2}\left\{-\frac{26}{5}k^2\bar{a}^2\right\} \\
&= 1-\frac{1}{5}k^2\bar{a}^2-\frac{13}{5}k^2\bar{a}^2\,\frac{\sigma^2}{\bar{a}^2}
\end{aligned}$$

Thus, for sufficiently small wave vectors, the form factor is equal to

$$\boxed{P^{pol}(k) \approx 1-\frac{1}{5}\left(k\bar{a}^2\right)\left[1+13\frac{\sigma^2}{\bar{a}^2}\right] \quad ; \quad k\bar{a} \ll 1}$$

3.8 Small polydispersity and dynamic light scattering: second cumulant analysis

The measured (or "polydisperse") EACF is equal to (see eqn.(3.105))

$$\hat{g}_E^{pol}(k,t) = \frac{\int_0^\infty da\, P_0(a)\, B^2(k,a) \exp\left(-D_0(a) k^2 t\right)}{\int_0^\infty da\, P_0(a)\, B^2(k,a)}$$

where $B(k,a)$ is the scattering amplitude and $P_0(a)$ is the size probability density function. For narrow size-distribution functions, the *a*-dependent functions (other than $P_0(a)$) can be expanded around the average value $\overline{a}$ of a . First rewrite the above expression as

$$\hat{g}_E^{pol}(k,t) = \exp\left(-D_0^{pol} k^2 t\right) \frac{\int_0^\infty da\, P_0(a)\, B^2(k,a) \exp\left(\left[D_0^{pol} - D_0(a)\right] k^2 t\right)}{\int_0^\infty da\, P_0(a)\, B^2(k,a)}$$

where the polydisperse diffusion coefficient will be defined later. For radii close to the average value, the polydisperse diffusion coefficient is close to $D_0(\overline{a})$. Hence we can expand

$$\exp\left(\left[D_0^{pol} - D_0(a)\right] k^2 t\right) \approx 1 - \left[D_0^{pol} - D_0(a)\right] k^2 t + \frac{1}{2}\left[D_0^{pol} - D_0(a)\right]^2 \left(k^2 t\right)^2 + \cdots$$

so that

$$\hat{g}_E^{pol}(k,t) = \exp\left(-D_0^{pol} k^2 t\right) \frac{\int_0^\infty da\, P_0(a)\, B^2(k,a) \left[1 - \left(D_0^{pol} - D_0(a)\right) k^2 t + \frac{1}{2}\left(D_0^{pol} - D_0(a)\right)^2 \left(k^2 t\right)^2 + \cdots\right]}{\int_0^\infty da\, P_0(a)\, B^2(k,a)}$$

$$= \exp\left(-D_0^{pol} k^2 t\right) \frac{\int_0^\infty da\, P_0(a)\, B^2(k,a) \left[1 + \frac{1}{2}\left(D_0^{pol} - D_0(a)\right)^2 \left(k^2 t\right)^2 + \cdots\right]}{\int_0^\infty da\, P_0(a)\, B^2(k,a)}$$

provided that the polydisperse diffusion coefficient is defined as

$$D_0^{pol}(k) = \frac{\int_0^\infty da\, P_0(a)\, B^2(k,a) D_0(a)}{\int_0^\infty da\, P_0(a)\, B^2(k,a)}$$

The standard deviation in the diffusion coefficient is now defined as

$$\sigma_D{}^2 = \frac{\int_0^\infty da P_0(a) B^2(k,a)\left(D_0(a) - D_0^{pol}(k)\right)^2}{\int_0^\infty da P_0(a) B^2(k,a)}$$

so that the above expression for the correlation function can be written as

$$\hat{g}_E^{pol}(k,t) = \exp\left(-D_0{}^{pol} k^2 t\right)\left[1 + \frac{1}{2} k^4 t^2 \sigma_D{}^2\right] = \exp\left(-D_0{}^{pol} k^2 t + \frac{1}{2} k^4 t^2 \sigma_D{}^2\right)$$

In order to express the polydisperse diffusion coefficient in terms of the size-standard deviation, we employ the Taylor expansion

$$\begin{aligned} & B^2(k,a) D_0(a) \\ & \approx B^2(k,\overline{a}) D_0(\overline{a}) + \left(a - \overline{a}\right)\frac{d}{d\overline{a}}\left[B^2(k,\overline{a}) D_0(\overline{a})\right] + \frac{1}{2}\left(a - \overline{a}\right)^2 \frac{d^2}{d\overline{a}^2}\left[B^2(k,\overline{a}) D_0(\overline{a})\right] \end{aligned}$$

The term $\sim \left(a - \overline{a}\right)$ vanishes by definition upon integration. A similar expansion must be made for the denominator in the expression for D_0^{pol}. Hence, to leading order in polydispersity

$$\begin{aligned} D_0^{pol}(k) & \approx \frac{B^2(k,\overline{a}) D_0(\overline{a}) + \frac{1}{2}\sigma^2 \frac{d^2}{d\overline{a}^2}\left(B^2(k,\overline{a}) D_0(\overline{a})\right)}{B^2(k,\overline{a})\left[1 + \frac{1}{2B^2(k,\overline{a})}\sigma^2 \frac{d^2}{d\overline{a}^2} B^2(k,\overline{a})\right]} \\ & \approx D_0(\overline{a}) + \left(\frac{\sigma}{\overline{a}}\right)^2 \frac{\overline{a}^2}{2B^2(k,\overline{a})}\left\{\frac{d^2}{d\overline{a}^2}\left(B^2(k,\overline{a}) D_0(\overline{a})\right) - D_0(\overline{a})\frac{d^2}{d\overline{a}^2} B^2(k,\overline{a})\right\} \end{aligned}$$

To leading order in the standard deviation σ^2, only the term $\sim \left(D_0(a) - D_0(\overline{a})\right)^2$, resulting after substitution of the above result into the defining expression for $\sigma_D{}^2$ contributes. Since $D_0(a) \sim 1/a$, we have

$$\frac{dD_0(a)}{da} = -\frac{D_0(a)}{a}$$

from which it thus follows that

$$\boxed{\frac{\sigma_D}{D_0(\overline{a})} = \frac{\sigma}{\overline{a}}}$$

Using that for small wave vectors $k\overline{a} < 1/2$, we have $B(k,\overline{a}) \sim \overline{a}^3$ and $\overline{a}D_0(\overline{a})$ is a constant, independent of the average radius, the above expression for D_0^{pol} leads to

$$D_0^{pol}(k) \approx D_0(\overline{a}) + \left(\frac{\sigma}{\overline{a}}\right)^2 \frac{\overline{a}^2}{2\overline{a}^6}\left\{\frac{d^2}{d\overline{a}^2}\left(\overline{a}^6 \frac{1}{\overline{a}}\left[\tilde{a}D_0(\overline{a})\right]\right) - D_0(\overline{a})\frac{d^2}{d\overline{a}^2}\overline{a}^6\right\}$$

Performing the differentiations finally gives

$$\boxed{D_0^{pol}(k) \approx D_0(\overline{a})\left[1-5\left(\frac{\sigma}{\overline{a}}\right)^2\right]}$$

Putting things together, we thus arrive at an expression for the measured, polydisperse correlation function in terms of the standard deviation in the radius

$$\boxed{\hat{g}_E^{pol}(k\to 0,t) = \exp\left\{-D_0(\overline{a})\left[1-5\left(\frac{\sigma}{\overline{a}}\right)^2\right]k^2 t + \frac{1}{2}D_0^2(\overline{a})\left(\frac{\sigma}{\overline{a}}\right)^2\left(k^2 t\right)^2\right\}}$$

This result enables the determination of the average radius and its standard deviation from a so-called second-cumulant fit, where a term $\sim k^4 t^2$ in the exponent is included in the fit to experimental data.

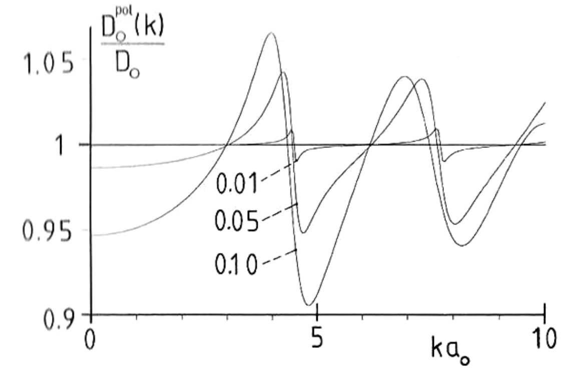


Fig. 3.12: The polydisperse diffusion coefficient, relative to the monodisperse diffusion coefficient $D_0(\overline{a})$, versus ka_0 for various values of the relative standard deviation $\sigma/\overline{a}$, as indicated by the numbers attached to the different curves. The radius a_0 is related to $\overline{a}$, as discussed in section 3.9.1 (see especially eqn.(3.102)).

3.11 Form factor of a thick rod

For static light scattering by thin rods, where $kD < 0.2$ the integral ranging over a cylinder with its geometrical center at the origin

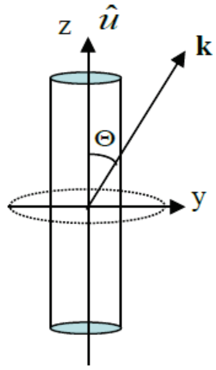
$$I \equiv \frac{1}{V}\int_{V_0} d\vec{r}\,\exp\left(i\vec{k}\cdot\vec{r}\right)$$

was calculated in subsection 3.10.2. Now suppose that kD is not small. Here we evaluate the form factor for that case where the rod has an arbitrary orientation of the rod.

The wave vector is now decomposed in its component $k_z = \vec{k}\cdot\hat{u}$ parallel to the rod, and $k_y = k\sqrt{1-\left(\vec{k}\cdot\hat{u}/k\right)^2}$ its component perpendicular to the rod's long axis. We can now write

$$\vec{k}\cdot\vec{r} = k\,y\sqrt{1-(\hat{k}\cdot\hat{u})^2} + k\,z\,(\hat{k}\cdot\hat{u})$$

where $\hat{k} = \vec{k}/k$ is the unit vector along $\vec{k}$. Note that the form factor only depends on the direction of the wave vector through its angle Θ with the *z*-axis (see the figure below).



The integral thus reads, in terms of cylindrical coordinates

$$I \equiv \frac{1}{V}\int_0^{2\pi} d\phi \int_{-L/2}^{L/2} dz \int_0^{D/2} d\rho\,\rho\exp\left\{i\left[kz(\hat{k}\cdot\hat{u}) + k\rho\sin\{\phi\}\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right]\right\}$$

The *z*-integral is relatively simple

$$\int_{-L/2}^{L/2} dz\,\exp\left\{ikz(\hat{k}\cdot\hat{u})\right\} = L\,\frac{\sin\left\{\frac{1}{2}Lk(\hat{k}\cdot\hat{u})\right\}}{\frac{1}{2}Lk(\hat{k}\cdot\hat{u})} \equiv L\,j_0\left(\frac{1}{2}Lk(\hat{k}\cdot\hat{u})\right)$$

where the last identity defines the spherical Bessel function of zeroth order.

For *n=0* we have

$$J_0(x) \equiv \frac{1}{\pi}\int_0^{\pi} d\phi \cos\left(x\sin\phi\right) = \frac{1}{2\pi}\int_0^{2\pi} d\phi \exp\left\{ix\sin\phi\right\}$$

so that

$$\int_0^{D/2} d\rho\rho \int_0^{2\pi} d\phi \exp\left\{ik\rho\sin\{\phi\}\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right\} = 2\pi \int_0^{D/2} d\rho\rho\, J_0\left(k\rho\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right)$$

Now using that

$$\frac{d}{dx}\left(xJ_1(x)\right) = xJ_0(x)$$

it follows that

$$\begin{aligned}
\int_0^{D/2} d\rho\rho\, J_0\left(k\rho\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right) &= \frac{1}{\left(k\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right)^2}\int_0^{\frac{1}{2}Dk\sqrt{1-(\hat{k}\cdot\hat{u})^2}} dx\, xJ_0(x) \\
&= \frac{1}{\left(k\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right)^2}\int_0^{\frac{1}{2}Dk\sqrt{1-(\hat{k}\cdot\hat{u})^2}} dx \frac{d}{dx}\left(xJ_1(x)\right) \\
&= \frac{D/2}{k\sqrt{1-(\hat{k}\cdot\hat{u})^2}} J_1\left(\frac{1}{2}Dk\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right)
\end{aligned}$$

Since the volume of the cylinder is equal to

$$V = \frac{\pi}{4}D^2 L$$

it is finally found that

$$\boxed{I = \frac{2J_1\left(\frac{1}{2}kD\sqrt{1-\left(\vec{k}\cdot\hat{u}/k\right)^2}\right)}{\frac{1}{2}kD\sqrt{1-\left(\vec{k}\cdot\hat{u}/k\right)^2}}\frac{\sin\left(\frac{1}{2}L\vec{k}\cdot\hat{u}\right)}{\frac{1}{2}L\vec{k}\cdot\hat{u}}}$$

3.12 Form factor of a thin rod

(a) The square root of the form factor of a cylindrical rod as obtained in exercise 3.11 is

$$I \equiv \frac{1}{V}\int_0^{2\pi} d\phi \int_{-L/2}^{L/2} dz \int_0^{D/2} d\rho\rho \exp\left\{ i\left[kz(\hat{k}\cdot\hat{u}) + k\rho\sin\{\phi\}\sqrt{1-(\hat{k}\cdot\hat{u})^2}\right]\right\}$$

In case of a thin rod, for which $kD \leq 0.2$ this is easily seen to reduce to

$$I \equiv \frac{2\pi}{V}\frac{D^2}{8}\int_{-L/2}^{L/2} dz \exp\left\{ikz(\hat{k}\cdot\hat{u})\right\} = \frac{\sin\left\{\frac{1}{2}Lk(\hat{k}\cdot\hat{u})\right\}}{\frac{1}{2}Lk(\hat{k}\cdot\hat{u})} \equiv j_0\left(\frac{1}{2}Lk(\hat{k}\cdot\hat{u})\right)$$

where the last identity defines the Bessel function j_0 , and it is used that $V = \frac{\pi}{4}D^2 L$.

Since the orientationally averaged form factor is independent of the direction of the wave vector, it may be chosen along the *z*-direction. Hence

$$\begin{aligned}
\left\langle j_0^{\,2}\left(\frac{1}{2}L\vec{k}\cdot\hat{u}\right)\right\rangle &= \frac{1}{4\pi}\oint d\hat{u}\, j_0^{\,2}\left(\frac{1}{2}L\vec{k}\cdot\hat{u}\right) \\
&= \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\Theta \sin\{\Theta\}\, j_0^{\,2}\left(\frac{1}{2}Lk\cos\{\Theta\}\right) \\
&= \frac{1}{2}\int_{-1}^{1} dx\, j_0^{\,2}\left(\frac{1}{2}Lkx\right) \\
&= \frac{2}{kL}\int_0^{kL/2} dz\, j_0^2(z) = \frac{2}{kL}\int_0^{kL/2} dz\left(\frac{\sin z}{z}\right)^2
\end{aligned}$$

where the new integration variables $x = \cos\{\Theta\}$ and $z = \frac{1}{2}Lkx$ have been introduced.

Contrary to the form factor of a sphere (see Fig.3.7), there is no scattering angle where total negative interference occurs. This is due to the fact that we have a system of "polydisperse scatterers", each species corresponding to a different orientation of the rods.

(b) For $kL < 1$, that is, small scattering angles, the integrand in the integral in exercise (a) can be expanded as

$$\frac{\sin z}{z} \approx 1 - \frac{1}{6} z^2$$

so that

$$\frac{2}{kL}\int_0^{kL/2} dz \left(\frac{\sin z}{z}\right)^2 \approx \frac{2}{kL}\int_0^{kL/2} dz \left(1 - \frac{1}{6} z^2\right)^2 \approx 1 - \frac{1}{36}(kL)^2 + \mathrm{O}((kL)^4)$$

Re-exponentiation thus leads to the scattered intensity being approximately equal to

$$\boxed{I \approx \exp\left\{-\frac{1}{36} L^2 k^2\right\}}$$

This is the equivalent of the Guinier approximation as discussed in detail in section 3.8.1 for spherical colloids. The slope of the Guinier plot for thin rods is thus equal to $-\frac{1}{36} L^2$.

3.13 Heterodyne dynamic light scattering

When the scattered light is mixed with incident light directed towards the detector, the detected electric field strength is

$$E^{het}(t) = E^{loc} + E_S(t)$$

where $E_s(t)$ is the field scattered by the particles, and E^{loc} is so-called "local oscillator" field strength from the incident field that is mixed with the scattered light. The instantaneous detected intensity is now

$$\begin{aligned} i(t) &\sim \left(E^{loc} + E_S(t)\right) * \left(E^{loc*} + E_S^*(t)\right) \\ &= I^{loc} + E_S(t)E^{loc*} + E^{loc}E_S^*(t) + E_S(t)E_S^*(t) \end{aligned}$$

The IACF for heterodyne light scattering is therefore equal to

$$\begin{aligned} \langle i(t)i(0)\rangle &= < \left(I^{loc} + E_S(t)E^{loc*} + E^{loc}E_S^*(t) + E_S(t)E_S^*(t)\right) \\ &\quad * \left(I^{loc} + E_S(0)E^{loc*} + E^{loc}E_S^*(0) + E_S(0)E_S^*(0)\right) > \\ &= \left(I^{loc}\right)^2 + I^{loc}\langle E_S(0)\rangle E^{loc*} + I^{loc}E^{loc}\left\langle E_S^*(0)\right\rangle + I^{loc}\left\langle E_S(0)E_S^*(0)\right\rangle \\ &\quad + \langle E_S(t)E_S(0)\rangle\left(E^{loc*}\right)^2 + I^{loc}\left\langle E_S(t)E_S^*(0)\right\rangle + I^{loc}\left\langle E_S^*(t)E_S(0)\right\rangle \\ &\quad + I^{loc}\, I + \left\langle E_S(t)E_S^*(t)E_S(0)E_S^*(0)\right\rangle \end{aligned}$$

where $I^{loc} \sim \left|E^{loc}\right|^2$ is the intensity of the light that is mixed in with the scattered light. Since the average of the oscillating field strength is zero

$$\langle E_S(0)\rangle = 0 = \left\langle E_S^*(0)\right\rangle$$

and the average scattered intensity is equal to $I \sim \left\langle E_S(0)E_S^*(0)\right\rangle$,while (see page 133-134 in the book)

$$\langle E_S(t)E_S(0)\rangle = 0$$

and

$$\left\langle E_S(t)E_S^*(t)E_S(0)E_S^*(0)\right\rangle = I^2 + \left|\left\langle E_S(0)E_S^*(t)\right\rangle\right|^2$$

with I the scattered intensity, this expression reduces to

$$\boxed{g_I^{het}(\vec{k},t) = \left(I^{loc}\right)^2 + 2I^{loc}I + I^2 + 2I^{loc}I\,\mathrm{Re}\left(\hat{g}_E(\vec{k},t)\right) + I^2\left|\hat{g}_E(\vec{k},t)\right|^2}$$

Note that for $I^{loc} > 50\,I$ this heterodyne IACF is approximately equal to the homodyne EACF.

3.14 For a very dilute system of Brownian spheres, where interactions between the colloids can be neglected, the pdf in the presence of a constant external field $\vec{F}$ is equal to (see exercise 2.4)

$$P(\vec{r}\,',t) = \frac{1}{\left(4\pi D_0 t\right)^{3/2}} \exp\left(-\left| \vec{r}\,' - \frac{\vec{F}}{\gamma} t \right|^2 / 4D_0 t \right)$$

where $\vec{r}\,'$ is the displacement during the time *t*. In case $I^{loc} \gg I$, according to the previous exercise, the heterodyne correlation function becomes equal to

$$g_I^{het}(\vec{k},t) = \left(I^{loc}\right)^2 + 2I^{loc} I \left[1 + \mathrm{Re}\left(\hat{g}_E(\vec{k},t) \right) \right]$$

The normalized electric field auto correlation function (EACF) is equal to

$$\hat{g}_E(\vec{k},t) = \int d\vec{r}\; P(\vec{r}\,',t) \exp\left(i\vec{k} \cdot \vec{r}\,' \right)$$

Introducing the new integration variable $\vec{R} = \vec{r}\,' - (\vec{F}/\gamma)t$, we arrive at

$$\hat{g}_E(\vec{k},t) = \frac{1}{\left(4\pi D_0 t\right)^{3/2}} \exp\left(i\vec{k} \cdot \vec{v} t \right) \int d\vec{R} \exp\left(-R^2 / 4D_0 t \right) \exp\left(i\vec{k} \cdot \vec{R} \right)$$

where $\vec{v} = \vec{F}/\gamma$ is the stationary velocity that the Brownian spheres attain under the action of the external force. According to the appendix in chapter 1, page 49, on integration of Gaussian functions, this leads to

$$\hat{g}_E(\vec{k},t) = \exp\left(i\vec{k} \cdot \vec{v} t \right) \exp\left(-D_0 k^2 t \right)$$

the real part of which is equal to

$$\hat{g}_E(\vec{k},t) = \cos\left(\vec{k} \cdot \vec{v} t \right) \exp\left(-D_0 k^2 t \right)$$

The measured heterodyne IACF is thus equal to

$$\boxed{g_I^{het} = \left(I^{loc}\right)^2 + 2I^{loc} I \left\{ 1 + \cos\left(\vec{k} \cdot \vec{v}\, t \right) \exp\left(-D_0 k^2 t \right) \right\}}$$

This correlation function is a damped exponential as depicted in the figure.

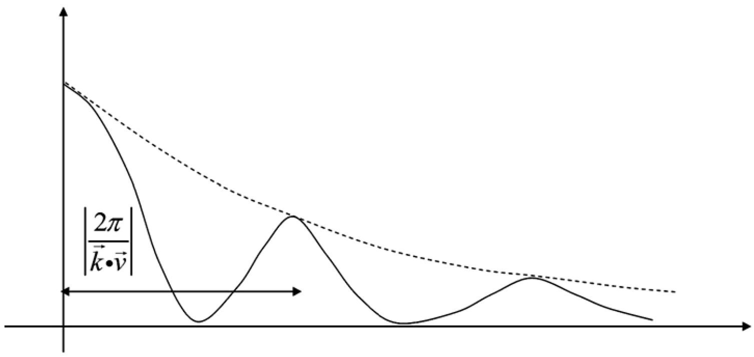


Fig.: A sketch of the heterodyne IACF

Setting I^{loc} in the equation for the IACF in the previous exercise equal to zero, it is immediately found that the homodyne correlation function is not affected by the velocity of the Brownian particles (since $\left|\exp\left(i\vec{k}\cdot\vec{v}t\right)\right|=1$).

Heterodyne light scattering is required in order to be able to measure particle velocities.

Exercises Chapter 4: FUNDAMENTAL EQUATIONS OF MOTION

4.2 The Brownian oscillator

Two identical Brownian spheres are connected to each other with a spring, corresponding to a potential energy

$$\Phi = \frac{1}{2} C \left| \vec{r}_1 - \vec{r}_2 \right|^2$$

where $\vec{r}_1$ and $\vec{r}_2$ are the position coordinates of the two spheres, and C is the spring constant.

Define the distance between the spheres $\vec{R} = \vec{r}_1 - \vec{r}_2$ and the center-of-mass position $\vec{r} = (\vec{r} + \vec{r}_2)/2$. Now, for example,

$$\nabla_{r_1} f(\vec{R} = \vec{r}_1 - \vec{r}_2, \vec{r} = (\vec{r}_1 + \vec{r}_2)/2) =$$
$$\left(\nabla_{r_1} \vec{R}\right) \cdot \nabla_R f(\vec{R}, \vec{r}) + \left(\nabla_{r_1} \vec{r}\right) \cdot \nabla_r f(\vec{R}, \vec{r}) = \left(\nabla_R - \frac{1}{2} \nabla_r\right) f(\vec{R}, \vec{r})$$

where $\left(\nabla_{r_1} \vec{R}\right)$ is the matrix with components *i* and *j* equal to the *i-th* component of ∇_{r_1} and the *j-th* component of $\vec{R}$, and similarly for $\left(\nabla_{r_1} \vec{r}\right)$ A similar calculation for the derivative with respect to $\vec{r}_2$ thus gives

$$\nabla_{r1} = \nabla_R + \frac{1}{2} \nabla_r \quad , \quad \nabla_{r2} = -\nabla_R + \frac{1}{2} \nabla_r$$

The Smoluchowski equation in (4.40, 41) for two particles (with the neglect of hydrodynamic interactions) thus reads in terms of the new coordinates

as
$$\frac{\partial}{\partial t} P\left(\vec{R},\vec{r},t\right) = D_0 \left\{ 2\beta C \nabla_R \cdot \left(\vec{R}P\right) + 2\nabla_R^2 P + \frac{1}{2}\nabla_r^2 P \right\}$$

Now substitute the separation variables $P(\vec{R},\vec{r},t) \equiv P(\vec{R},t)P(\vec{r},t)$ to obtain

$$\frac{\partial}{\partial t} P\left(\vec{R},\vec{r},t\right) = P(\vec{R},t)\frac{\partial P\left(\vec{r},t\right)}{\partial t} + P(\vec{r},t)\frac{\partial P(\vec{R},t)}{\partial t}$$
$$= D_0 \left\{ P(\vec{R},t)\left[\frac{1}{2}\nabla_r^{\,2} P\left(\vec{r},t\right)\right] + P(\vec{r},t)\left[2\beta C \nabla_R \cdot \left(\vec{R}P(\vec{R},t)\right) + 2\nabla_R^2 P(\vec{R},t)\right]\right\}$$

Dividing both sides with $P(\vec{R},t)P(\vec{r},t)$ and equalizing the independent terms depending only on $\vec{r}$ and $\vec{R}$ gives

$$\frac{\partial P\left(\vec{R},t\right)}{\partial t} = D_0 \left\{ \left[2\beta C \nabla_R \cdot \left(\vec{R}P(\vec{R},t)\right) + 2\nabla_R^2 P(\vec{R},t)\right]\right\}$$

$$\frac{\partial P\left(\vec{r},t\right)}{\partial t} = \frac{1}{2} D_0 \nabla_r^{\,2} P(\vec{r},t)$$

The center-of-mass thus diffuses as a free single Brownian sphere with a diffusion coefficient equal to half of that of a single sphere. The interesting part of this result is the equation of motion for $P(\vec{R},t)$. Comparing this equation of motion with eqn. (4.59) we have the identification

$$\vec{A} = -2D_0 \beta C\, \hat{I}$$
$$\vec{B} = -2D_0 \hat{I}$$

and $\vec{X} = \vec{R}$. The corresponding equations of motion in (4.58, 59) are

$$\frac{d}{dt}\vec{m} = -2D_0 \beta C\, \vec{m},$$
$$\frac{d}{dt}\vec{M} = 4D_0\, \hat{I} - 4D_0 \beta C\, \vec{M}$$

where, as inferred at the top of page189,

$$\vec{m}(t) = < \vec{R} > (t)$$
$$\vec{M}(t) = < \left(\vec{R} - \vec{m}\right)\left(\vec{R} - \vec{m}\right) > (t)$$

The initial conditions are $\vec{m}(t=0) = \vec{R}_0$, $\vec{M}(t=0) = \vec{0}$

The solution for $\vec{m}(t)$ is simply equal to

$$\vec{m}(t) = \left\langle \vec{R} \right\rangle (t) = \vec{R}_0 \, e^{-2D_0 \beta C t}$$

The solution of the equation of motion for $\vec{M}$ is obtained by "the method of variation of constant" (see also exercise 2.1). First solve the homogeneous equation,

$$\frac{d}{dt} \vec{M} = -4D_0 \beta C \, \vec{M}$$

The solution of which reads

$$\vec{M} = \vec{K} \; e^{-4D_0 \beta C t}$$

where $\vec{K}$ is an integration constant. We now make this constant a function of time (hence the name "variation of constant"), such that the full inhomogeneous equation is satisfied. Substitution into the equation of motion gives

$$\frac{d}{dt} \vec{M} = e^{-4D_0 \beta C t} \frac{d\vec{K}(t)}{dt} - 4D_0 \beta C \, t \, \vec{K}(t) \, e^{-4D_0 \beta C t}$$

$$= 4D_0 \, \hat{I} - 4D_0 \beta C \, \vec{M} = 4D_0 \, \hat{I} - 4D_0 \beta C \, \vec{K}(t) \, e^{-4D_0 \beta C t}$$

so that

$$\frac{d\vec{K}(t)}{dt} = 4D_0 \, \hat{I} \, e^{+4D_0 \beta C t}$$

and hence

$$\vec{K}(t) = \vec{K}(0) + 4D_0 \, \hat{I} \int_0^t dt' \, e^{+4D_0 \beta C t'} \; = \vec{K}(0) + \frac{1}{\beta C} \hat{I} \left[e^{+4D_0 \beta C t} - 1 \right]$$

We thus finally find that

$$\vec{M}(t) = \frac{1}{\beta C} \hat{I} \left[1 - e^{-4D_0 \beta C t} \right]$$

where we used the initial condition, which implies that $\vec{K}(0) = \vec{0}$. The mean squared displacement is thus found to be equal to

$$\left\langle (\vec{R} - \vec{R}_0)(\vec{R} - \vec{R}_0) \right\rangle (t) = \frac{1}{\beta C} \hat{I} \left[1 - e^{-4D_0 \beta C t} \right] + \vec{R}(0) \vec{R}(0) \left[1 - e^{-2D_0 \beta C t} \right]^2$$

Note that there is an erroneous factor of 2 in the exponent in the given solution in the book. Since the Hamiltonian of this Brownian spring is quadratic in R, since $\Phi = (C R^2)/2$, it is expected that (see exercise 2.2) $\left\langle R_i R_j \right\rangle (t \to \infty) = \delta_{ij} / (\beta C)$, which is in accordance with the above result (rewritten in terms of $\left\langle \vec{R}\vec{R} \right\rangle$).

4.3 Diffusion in an inhomogeneous solvent

For very dilute homogeneous suspensions, the diffusion coefficient is equal to

$$D_0 = \frac{1}{\beta\gamma} = \frac{k_B T}{6\pi\eta_0 a}$$

Now consider an inhomogeneous solvent, so that the diffusion coefficient is different at each position. Since there is now a direction that is associated with the inhomogeneities, the diffusion coefficient is not a scalar but rather a tensorial quantity. The flux is now equal to $-\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t)$, so that the Smoluchowski equation is

$$\frac{\partial}{\partial t} P(\vec{r},t) = \nabla_r \cdot \left[\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t) \right]$$

The average velocity is

$$\frac{d\langle \vec{r} \rangle}{dt} = \int d\vec{r}\, \vec{r} \frac{\partial}{\partial t} P\left(\vec{r},t\right) = \int d\vec{r}\, \vec{r} \nabla_r \cdot \left(\vec{\vec{D}}_0(\vec{r}) \cdot P(\vec{r},t) \right)$$

The integral can be rewritten, using Gauss's integral theorem, with the neglect of surface contributions

$$\begin{aligned} Int &\equiv \int d\vec{r}\, \vec{r}\, \nabla_r \cdot \left[\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t) \right] = -\int d\vec{r} \left[\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t) \right] \cdot \left(\nabla_r \vec{r} \right) \\ &= -\int d\vec{r} \left[\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t) \right] \cdot \left(\hat{I} \right) = -\int d\vec{r} \left[\vec{\vec{D}}_0(\vec{r}) \cdot \nabla_r P(\vec{r},t) \right] \end{aligned}$$

Applying Gauss's integral theorem once more gives

$$Int = \int d\vec{r}\, P(\vec{r},t) \left[\nabla_r \cdot \vec{\vec{D}}_0^T(\vec{r}) \right] = \left\langle \nabla_r \cdot \vec{\vec{D}}_0^T(\vec{r}) \right\rangle$$

Hence, the velocity induced by the inhomogeneous solvent is equal to

$$\frac{d}{dt} \langle \vec{r} \rangle = \left\langle \nabla_r \cdot \vec{\vec{D}}_0^T(\vec{r}) \right\rangle$$

As an example, consider a solvent that consists of a mixture of water and ethanol, where the composition changes in the x-direction, say. This leads to a spatial change of the viscosity. In this case

$$\nabla_r \cdot \vec{\vec{D}}_0^T(\vec{r}) = \hat{e}_x \frac{d}{dx} \left(\frac{k_B T}{6\pi\eta_0(x) a} \right) = -\hat{e}_x \frac{k_B T}{6\pi\eta_0(x)^2 a} \frac{d\eta_0(x)}{dx} = -\hat{e}_x D_0(x) \frac{d \ln \eta_0(x)}{dx}$$

where $\hat{e}_x$ is the unit vector along the x-direction. To leading order in spatial gradients, in the evaluation of the average, the pdf can simply be taken as a constant, so that the velocity is equal to

$$\vec{v}(x) = -\hat{e}_x D_0(x) \frac{d \ln \eta_0(x)}{dx}$$

Note that the particle moves from regions of high viscosity to regions of low viscosity.

(a) For spherical particles, the hydrodynamic torques are zero in the absence of an external field. From eqn.(4.128)

$$\begin{pmatrix} \vec{F}_1^h \\ \vdots \\ \vec{F}_N^h \\ \vec{\tau}_1^h \\ \vdots \\ \vec{\tau}_N^h \end{pmatrix} = -\begin{pmatrix} \vec{\vec{\gamma}}^{TT} & \vec{\vec{\gamma}}^{TR} \\ \vec{\vec{\gamma}}^{RT} & \vec{\vec{\gamma}}^{RR} \end{pmatrix} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \\ \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix}$$

Since the torque on the sphere is zero, this implies that

$$\begin{pmatrix} \vec{F}_1^h \\ \vdots \\ \vec{F}_N^h \\ \vec{0} \\ \vdots \\ \vec{0} \end{pmatrix} = -\begin{pmatrix} \vec{\vec{\gamma}}^{TT} & \vec{\vec{\gamma}}^{TR} \\ \vec{\vec{\gamma}}^{RT} & \vec{\vec{\gamma}}^{RR} \end{pmatrix} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \\ \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix}$$

and hence

$$\begin{pmatrix} \vec{F}_1^h \\ \vdots \\ \vec{F}_N^h \end{pmatrix} = -\vec{\vec{\gamma}}^{TT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix} - \vec{\vec{\gamma}}^{TR} \cdot \begin{pmatrix} \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix} \quad , \quad \begin{pmatrix} \vec{0} \\ \vdots \\ \vec{0} \end{pmatrix} = -\vec{\vec{\gamma}}^{RT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix} - \vec{\vec{\gamma}}^{RR} \cdot \begin{pmatrix} \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix}$$

From the last equation it follows that the orientational velocities are equal to

$$\begin{pmatrix} \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix} = -\left(\vec{\vec{\gamma}}^{RR}\right)^{-1} \cdot \vec{\vec{\gamma}}^{RT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix}$$

Substitution into the above equation for the forces gives

$$\begin{pmatrix} \vec{F}_1^h \\ \vdots \\ \vec{F}_N^h \end{pmatrix} = -\vec{\vec{\gamma}}^{TT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix} - \vec{\vec{\gamma}}^{TR} \cdot \begin{pmatrix} \vec{\Omega}_1 \\ \vdots \\ \vec{\Omega}_N \end{pmatrix} = -\vec{\vec{\gamma}}^{TT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix} + \vec{\vec{\gamma}}^{TR} \cdot \left(\vec{\vec{\gamma}}^{RR}\right)^{-1} \cdot \vec{\vec{\gamma}}^{RT} \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix}$$

$$= \left[-\vec{\vec{\gamma}}^{TT} + \vec{\vec{\gamma}}^{TR} \cdot \left(\vec{\vec{\gamma}}^{RR}\right)^{-1} \cdot \vec{\vec{\gamma}}^{RT} \right] \cdot \begin{pmatrix} \vec{v}_1 \\ \vdots \\ \vec{v}_N \end{pmatrix}$$

(b) As a sphere translates through a fluid, they transfer energy to the fluid. Since energy E is "distance times force", we have for the energy per unit time dissipated to the solvent

$$\frac{dE}{dt} = (frictional\ force) * \left(\frac{dis\tan ce}{time}\right) = (frictional\ force) * (velocity)$$

where the frictional force is the force that all the particles exert onto the solvent, which is minus $\vec{F}_j^h$. Hence

$$\frac{dE}{dt} = -\sum_{i=1}^{N} \vec{F}_i^h \cdot \vec{v}_i > 0$$

Since the velocity is equal to

$$\vec{v}_i = -\beta \sum_{j=1}^{N} \vec{\vec{D}}_{ij} \cdot \vec{F}_j^h$$

it follows that

$$\sum_{j=1}^{N} \vec{F}_i^h \cdot \vec{\vec{D}}_{ij} \cdot \vec{F}_j^h > 0$$

Introducing the abbreviations

$$\vec{x} = \left(\vec{F}_1^h, \cdots, \vec{F}_N^h\right)$$

and the *3Nx3N* dimensional diffusion tensor

$$\vec{\vec{D}}_{ij} = \begin{pmatrix} \vec{\vec{D}}_{11} & \cdots & \vec{\vec{D}}_{1N} \\ \vdots & \ddots & \vdots \\ \vec{\vec{D}}_{N1} & \cdots & \vec{\vec{D}}_{NN} \end{pmatrix}$$

it is thus found that

$$\boxed{\vec{x} \cdot \vec{\vec{D}} \cdot \vec{x} > 0}$$

for any $\vec{x} \neq \vec{0}$. A tensor with this property is referred to as "positive definite".

4.5 The direct torque on a rod

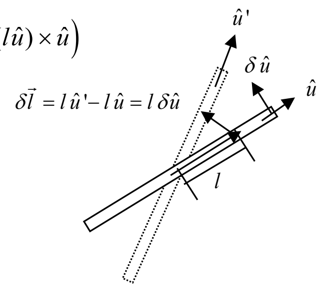
Consider a very thin and long rod, the core of which we approximate as a line. Let l be the contour variable, $-L/2 \le l \le L/2$. The position of a line element on the core is given by $l\hat{u}$, where $\hat{u}$ is the orientation of the rod.

Let $\vec{f}(\vec{r} = l\hat{u})$ be the force on line elements (either due to an external field and/or interactions with other rods). When the orientation of the rod is changed by a small amount $\delta\hat{u}$, the accompanied change in potential energy is (see the figure)

$$\delta\Phi = -\int_{-L/2}^{L/2} dl\, \vec{f}(l\hat{u}) \cdot \left(l\delta\hat{u}\right)$$

Using that $\vec{a} \times (\vec{b} \times \vec{c}) = (\vec{a} \cdot \vec{c})\,\vec{b} - (\vec{a} \cdot \vec{b})\,\vec{c}$, $\hat{u} \perp \delta\hat{u}$, and $\vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{c} \cdot (\vec{a} \times \vec{b})$, it is easily verified that,

$$\delta\Phi = -\int_{-L/2}^{L/2} dl\, l\, \vec{f}(l\hat{u}) \cdot \left(\hat{u} \times \left(\delta\hat{u} \times \hat{u}\right)\right) = -\left(\delta\hat{u} \times \hat{u}\right) \cdot \int_{-L/2}^{L/2} dl\, l\left(\vec{f}(l\hat{u}) \times \hat{u}\right)$$
$$\equiv \left(\delta\hat{u} \times \hat{u}\right) \cdot \vec{\tau} = \delta\hat{u} \cdot \left(\hat{u} \times \vec{\tau}\right)$$



where $\vec{\tau}$ is the torque, which is equal to

$$\vec{\tau} \equiv \int_{V_0} d\vec{r}\, \vec{r} \times \vec{f}(\vec{r}) \approx \hat{u} \times \int_{-L/2}^{L/2} dl\, \left[l\hat{u} \times \vec{f}(l\hat{u})\right]$$

The first equation defines the torque (with V_0 the volume occupied by the core), while in the second equation its approximation for the very long and thin rod is given.

On the other hand we have $\delta\Phi = \delta\hat{u} \cdot \nabla_u \Phi$, where ∇_u is the gradient operator with respect to the Cartesian coordinates of $\hat{u}$. Comparing to the above result we thus have

$$\delta\Phi = \delta\hat{u} \cdot \nabla_u \Phi = \delta\hat{u} \cdot (\hat{u} \times \vec{\tau})$$

Since $\delta\hat{u}$ is an arbitrary vector, but always lies in the plane perpendicular to $\hat{u}$, the conclusion is that the components of $\nabla_u \Phi$ and $\hat{u} \times \vec{\tau}$ in that plane are equal.

The vectors are thus equal when they do not have a component along $\hat{u}$. For $\hat{u} \times \vec{\tau}$ this is immediately clear, since it is perpendicular to $\hat{u}$. That $\nabla_u \Phi$ is also perpendicular to $\hat{u}$ follows from $\hat{u} \cdot \nabla_{\hat{u}} \Phi = d\Phi / d\left|\hat{u}\right| = 0$, since $\hat{u}$ is constrained to have a fixed length of unity. Hence

$$\nabla_{\hat{u}} \Phi = \hat{u} \times \vec{\tau}$$

Taking the outer product of both sides, noting that $\vec{\tau}$ is perpendicular to $\hat{u}$, and using the above relation for an outer product of three vectors, leads to

$$\vec{\tau} = -\hat{u} \times \nabla_{\hat{u}} \Phi \equiv -\hat{R}\Phi$$

with $\hat{R}$ the rotational operator. This is the rotational analogue of the translational result $\vec{F} = -\nabla\Phi$ for the force.

4.6 To evaluate $\nabla_r^2 \vec{r}\vec{r}$ the following steps can be made

$$\nabla_r^2 r_i r_j = \sum_{n=1}^{3} \frac{\partial^2}{\partial r_n{}^2}\left(r_i r_j\right) = \sum_{n=1}^{3} \frac{\partial}{\partial r_n}\left(r_i \delta_{nj} + r_j \delta_{ni}\right)$$

$$= \sum_{n=1}^{3}\left(\delta_{in}\delta_{nj} + \delta_{jn}\delta_{ni}\right)$$

$$= 2\sum_{n=1}^{3}\left(\delta_{in}\delta_{nj}\right) = 2\delta_{ij}$$

The components of the rotational operator are, by definition

$$\hat{R} \equiv \hat{u} \times \nabla_{\hat{u}} = \begin{pmatrix} u_2\partial_3 - u_3\partial_2 \\ u_3\partial_1 - u_1\partial_3 \\ u_1\partial_2 - u_2\partial_1 \end{pmatrix}$$

where the partials denote differentiation, $\partial_j = \left(\nabla_{\hat{u}}\right)_j$, that is, ∂_j is the differentiation with respect to the j^{th} component of $\hat{u}$. Since

$$\hat{R}^2\,\hat{u} = \sum_{n=1}^{3}[\hat{R}\cdot\hat{R}]\,\hat{u} = \sum_{n=1}^{3}\,[\left(\hat{u}\times\nabla_{\hat{u}}\right)\cdot\left(\hat{u}\times\nabla_{\hat{u}}\right)]\hat{u}$$

and

$$\hat{R}\,\hat{u}_1 = \begin{pmatrix} \hat{u}_2\partial_3 - \hat{u}_3\partial_2 \\ \hat{u}_3\partial_1 - \hat{u}_1\partial_3 \\ \hat{u}_1\partial_2 - \hat{u}_2\partial_1 \end{pmatrix}\hat{u}_1 = \begin{pmatrix} 0 \\ \hat{u}_3 \\ -\hat{u}_2 \end{pmatrix}$$

which follows from the above component-wise representation of the rotation operator, we have

$$\hat{R}^2\,\hat{u}_1 = \sum_{n=1}^{3}\hat{R}_n\left(\hat{R}_n\,\hat{u}_1\right) = \hat{R}_1\cdot 0 + \hat{R}_2\cdot\hat{u}_3 - \hat{R}_3\cdot\hat{u}_2$$

From the same component-wise representation, it also follows that

$$\hat{R}_2\cdot\hat{u}_3 = \left(\hat{u}_3\partial_1 - \hat{u}_1\partial_3\right)\cdot\hat{u}_3 = -\hat{u}_1$$

$$\hat{R}_3\cdot\hat{u}_2 = \left(\hat{u}_1\partial_2 - \hat{u}_2\partial_1\right)\cdot\hat{u}_2 = \hat{u}_1$$

so that

$$\hat{R}^2\,\hat{u}_1 = -\hat{u}_1 - \hat{u}_1 = -2\hat{u}_1$$

The other components are calculated similarly, leading to $\hat{R}^2\,\hat{u} = -2\hat{u}$.

For an arbitrary vector $\vec{a}$ the i^{th} component of $\vec{a}\cdot\hat{R}\hat{u}$ is

$$\vec{a}\cdot\hat{R}\hat{u}_i \equiv \left[\vec{a}\cdot\left(\hat{u}\times\nabla_{\hat{u}}\right)\right]\hat{u}_i = \sum_{n=1}^{3} a_n\left(\hat{u}\times\nabla_{\hat{u}}\right)_n \hat{u}_i$$

For the different values of i, this is, according to the component-wise notation of the rotation operator

$$\begin{aligned}
i=1;&\quad a_1\cdot 0 + a_2\cdot(\hat{u}_3) + a_3\cdot\left(-\hat{u}_2\right) = a_2\cdot(\hat{u}_3) - a_3\cdot\left(\hat{u}_2\right)\\
i=2;&\quad a_1\cdot\left(-\hat{u}_3\right) + a_2\cdot 0 + a_3\cdot\left(\hat{u}_1\right) = a_3\cdot(\hat{u}_1) - a_1\cdot\left(\hat{u}_3\right)\\
i=3;&\quad a_1\cdot\left(\hat{u}_2\right) + a_2\cdot\left(-\hat{u}_1\right) + a_3\cdot 0 = a_1\cdot(\hat{u}_2) - a_2\cdot\left(\hat{u}_1\right)
\end{aligned}$$

so that

$$\vec{a}\cdot\hat{R}\,\hat{u} = \begin{pmatrix} a_2\cdot\hat{u}_3 - a_3\cdot\hat{u}_2 \\ a_3\cdot\hat{u}_1 - a_1\cdot\hat{u}_3 \\ a_1\cdot\hat{u}_2 - a_2\cdot\hat{u}_1 \end{pmatrix} = \vec{a}\times\hat{u}$$

This concludes the proof of the three identities

$$\boxed{\begin{aligned}&\nabla^2\vec{r}\vec{r} = 2\hat{I}\\ &\hat{R}^2\hat{u} = -2\hat{u}\\ &\vec{a}\cdot\hat{R}\,\hat{u} = \vec{a}\times\hat{u}\end{aligned}}$$

These and other identities are necessary for calculations of ensemble averages

4.7 Small angle depolarized time resolved static light scattering by rods

In this exercise we consider a dilute suspension of a rigid, rod like Brownian particles which are strongly aligned in the z-direction by means of an external field. The external field is turned off at time $t = 0$. After a long time the rods attain an isotropic distribution. We are considering here the kinetics of relaxation to the isotropic state after turning off the external field. Experimentally, the rotational relaxation kinetics can be measured by means of depolarized light scattering. The polarization direction $\hat{n}_0$ of the incident light is chosen in the *z*-direction, which is along the direction of alignment of the rods at time zero. The polarization direction $\hat{n}_s$ of the detected light is chosen in the *x*-direction.

We consider small angle light scattering such that $kL < 1$, where k is the wave vector and L is the length of the rods. The ensemble averaged scattered intensity is given by eqn (3.131) for the anisotropic structure factor

$$R \sim S^{(a,a)}(k) = \frac{1}{N}\sum_{i,j=1}^{N}\left\langle \begin{array}{c}(\hat{n}_s \cdot \hat{u}_i)(\hat{n}_s \cdot \hat{u}_j)(\hat{n}_0 \cdot \hat{u}_i)(\hat{n}_0 \cdot \hat{u}_j) \\ \times \dfrac{j_0\left(\frac{1}{2}L\vec{k}\cdot\hat{u}_i\right) j_0\left(\frac{1}{2}L\vec{k}\cdot\hat{u}_j\right)}{\left\langle j_0^2\left(\frac{1}{2}L\vec{k}\cdot\hat{u}\right)\right\rangle} \exp\left[i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)\right]\end{array}\right\rangle$$

For $kL < 1$, the Bessel functions are essentially equal to unity; while for non-interacting rods only the term where $i = j$ survive. Hence

$$R \sim \left\langle \hat{u}_z^2\, \hat{u}_x^2 \right\rangle$$

The scattered intensity is thus a strong function of the orientations. Since these change with time, the scattered intensity R is time dependent, which characterizes the relaxation of orientational order.

The time dependence of this depolarized small angle scattered intensity is calculated form the Smoluchowski equation

$$\frac{\partial}{\partial t} P(\vec{r},\hat{u},t) = \hat{L}_S^0\, P(\vec{r},\hat{u},t),$$

$$\hat{L}_S^0(\cdots) = \bar{D}\nabla_r^2(\cdots) + D_r\hat{\Re}^2(\cdots) + \Delta D\nabla_r \cdot \left[\hat{u}\hat{u} - \frac{1}{3}\hat{I}\right]\cdot\nabla_r(\cdots)$$

Since the quantity $\hat{u}_z^2\, \hat{u}_x^2$ is independent of the position coordinates of the rods, according to Gauss's integral theorem, only the rotational contribution $D_r\hat{\Re}^2$ in the Smoluchowski operator L_S^0 contributes. Multiplying both sides of the Smoluchowski equation by $\hat{u}_z^2\,\hat{u}_x^2$, and integrating, we thus arrive at the following expression for the time dependence of the scattered intensity

$$\frac{d}{dt}R = D_r \oint d\hat{u}\,\hat{u}_3^2\,\hat{u}_1^2\,\hat{\Re}^2 P(\hat{u},t) = D_r \oint d\hat{u}\,P(\hat{u},t)\,\hat{\Re}^2(\hat{u}_3^2\,\hat{u}_1^2)$$

where the integral ranges over all orientations of $\hat{u}$, and we replaced the indices *z* by *3* and *x* by *1* (and later we will replace *y* by *2*). In the last line we used Stokes's theorem in the form

$$\oint d\hat{u}\,f(\hat{u})\Re^2 g(\hat{u}) = \oint d\hat{S}\,g(\hat{u})\Re^2 f(\hat{u})$$

Using the same steps as in exercise 4.6, we find with some effort that

$$\begin{aligned}\hat{\Re}^2(\cdots) = \Big\{&\left(\hat{u}_2^2+\hat{u}_3^2\right)\partial_1^2+\left(\hat{u}_1^2+\hat{u}_3^2\right)\partial_2^2+\left(\hat{u}_1^2+\hat{u}_2^2\right)\partial_3^2\\ &-2\left[\hat{u}_2\hat{u}_3\partial_2\partial_3+\hat{u}_1\hat{u}_3\partial_1\partial_3+\hat{u}_1\hat{u}_2\partial_1\partial_2\right]\\ &-2\left[\hat{u}_1\partial_1+\hat{u}_2\partial_2+\hat{u}_3\partial_3\right]\ \Big\}(\cdots)\end{aligned}$$

The details of the derivation of this result are given at the end of this exercise. Here, ∂_j is the gradient operator with respect to the j^{th} component of $\hat{u}$. It is thus found that

$$\frac{d}{dt}\left\langle \hat{u}_3^2\hat{u}_1^2\right\rangle = D_r\left[-20\left\langle \hat{u}_3^2\hat{u}_1^2\right\rangle + 2\left(1-\left\langle \hat{u}_2^2\right\rangle\right)\right]$$

In order to explicitly solve this equation, we need an expression for $<\hat{u}_2^2>$. This can be obtained similarly as the above expression, by multiplying both sides of the Smoluchowski equation by $\hat{u}_2^2$, and integrate

$$\frac{d}{dt}\left\langle \hat{u}_2^2\right\rangle = D_r\oint d\hat{u}\ \hat{u}_2^2\,\hat{\Re}^2 P\left(\hat{u},t\right) = D_r\oint d\hat{u}\,P\left(\hat{u},t\right)\hat{\Re}^2\hat{u}_2^2$$

Again using the above expression for $\hat{\Re}^2$, it is found that

$$\frac{d}{dt}\left\langle \hat{u}_2^2\right\rangle = D_r\left[2-6\left\langle \hat{u}_2^2\right\rangle\right]$$

This equation can be integrated by means of "variation of constants" (see exercise 2.1; details are also given at the end of exercise)

$$\left\langle \hat{u}_2^2\right\rangle = \frac{1}{3}\left(1-e^{-6D_r t}\right)$$

Substitution into the equation of motion for $\hat{u}_3^2\,\hat{u}_1^2$, which can be integrated by "variation of constants", to give (details are again given later in this exercise)

$$\boxed{R\sim\left\langle \hat{u}_3^2\hat{u}_1^2\right\rangle = \frac{1}{15}+\frac{1}{21}e^{-6D_r t}-\frac{4}{35}e^{-20D_r t}}$$

This equation describes the time dependence of the depolarized, small angle scattered intensity during orientational relaxation.

Let us now discuss the mathematical details (i) for the derivation of the explicit result for the squared rotational operator, and (ii) on "variation of constants" for the integration of the equations of motion for $<\hat{u}_2^2>$ and $<\hat{u}_3^2\,\hat{u}_1^2>$.

The rotational operator is, by definition, equal to,

$$\hat{\Re} = \begin{pmatrix} \hat{u}_2\partial_3 - \hat{u}_3\partial_2 \\ \hat{u}_3\partial_1 - \hat{u}_1\partial_3 \\ \hat{u}_1\partial_2 - \hat{u}_2\partial_1 \end{pmatrix}$$

and hence

$$\begin{aligned}\hat{\Re}^2 = \sum_{n=1}^{3} \hat{\Re}_n\,\hat{\Re}_n \;&= \left(\hat{u}_2\partial_3 - \hat{u}_3\partial_2\right)\left(\hat{u}_2\partial_3 - \hat{u}_3\partial_2\right) \\ &+ \left(\hat{u}_3\partial_1 - \hat{u}_1\partial_3\right)\left(\hat{u}_3\partial_1 - \hat{u}_1\partial_3\right) \\ &+ \left(\hat{u}_1\partial_2 - \hat{u}_2\partial_1\right)\left(\hat{u}_1\partial_2 - \hat{u}_2\partial_1\right)\end{aligned}$$

Now

$$\begin{aligned}\left(\hat{u}_2\partial_3 - \hat{u}_3\partial_2\right)\left(\hat{u}_2\partial_3 - \hat{u}_3\partial_2\right) &= \hat{u}_2^{\,2}\partial_3^{\,2} - \hat{u}_2\partial_3\left(\hat{u}_3\partial_2\right) - \hat{u}_3\partial_2\left(\hat{u}_2\partial_3\right) + \hat{u}_3^{\,2}\partial_2^{\,2} \\ &= \hat{u}_2^{\,2}\partial_3^{\,2} - \hat{u}_2\partial_2 - \hat{u}_2\hat{u}_3\partial_3\partial_2 - \hat{u}_3\partial_3 - \hat{u}_3\hat{u}_2\partial_2\partial_3 + \hat{u}_3^{\,2}\partial_2^{\,2}\end{aligned}$$

and similarly

$$\left(\hat{u}_3\partial_1 - \hat{u}_1\partial_3\right)\left(\hat{u}_3\partial_1 - \hat{u}_1\partial_3\right) = \hat{u}_3^{\,2}\partial_1^{\,2} - \hat{u}_3\partial_3 - \hat{u}_3\hat{u}_1\partial_1\partial_3 - \hat{u}_1\partial_1 - \hat{u}_1\hat{u}_3\partial_3\partial_1 + \hat{u}_1^{\,2}\partial_3^{\,2}$$

$$\left(\hat{u}_1\partial_2 - \hat{u}_2\partial_1\right)\left(\hat{u}_1\partial_2 - \hat{u}_2\partial_1\right) = \hat{u}_1^{\,2}\partial_2^{\,2} - \hat{u}_1\partial_1 - \hat{u}_1\hat{u}_2\partial_2\partial_1 - \hat{u}_2\partial_2 - \hat{u}_2\hat{u}_1\partial_1\partial_2 + \hat{u}_2^{\,2}\partial_1^{\,2}$$

Adding these three terms leads to the expression that we used for the squared rotational operator (note also that $\hat{u}_1^2 + \hat{u}_2^2 + \hat{u}_3^2 = 1$)

$$\boxed{\begin{aligned}\hat{\Re}^2\left(\cdots\right) = \Big\{&\left(\hat{u}_2^2 + \hat{u}_3^2\right)\partial_1^2 + \left(\hat{u}_1^2 + \hat{u}_3^2\right)\partial_2^2 + \left(\hat{u}_1^2 + \hat{u}_2^2\right)\partial_3^2 \\ &- 2\left[\hat{u}_2\hat{u}_3\partial_2\partial_3 + \hat{u}_1\hat{u}_3\partial_1\partial_3 + \hat{u}_1\hat{u}_2\partial_1\partial_2\right] \\ &- 2\left[\hat{u}_1\partial_1 + \hat{u}_2\partial_2 + \hat{u}_3\partial_3\right]\ \Big\}\left(\cdots\right)\end{aligned}}$$

Next consider the equation of motion

$$\frac{d}{dt}\left\langle \hat{u}_2^2 \right\rangle = D_r\left[2 - 6\left\langle \hat{u}_2^2 \right\rangle\right]$$

The homogeneous equation reads

$$\frac{d}{dt}\left\langle \hat{u}_2^2 \right\rangle = -6D_r \left\langle \hat{u}_2^2 \right\rangle$$

the solution of which reads

$$\left\langle \hat{u}_2^2 \right\rangle = A\, e^{-6D_r t}$$

The integration constant A is now considered a function of time (hence the name "variation of constants"), such that it satisfies the full equation of motion. One finds after substitution

$$\frac{d}{dt} A(t) = 2D_r\, e^{+6D_r t}$$

Hence

$$A(t) = A_0 + \frac{1}{3}\left(e^{+6D_r t} - 1\right)$$

Since at time zero we have $\left\langle \hat{u}_2^2 \right\rangle = 0$ it follows that the initial value of A is zero: $A(t=0) \equiv A_0 = 0$. Thus

$$\left\langle \hat{u}_2^2 \right\rangle = \frac{1}{3}\left(1 - e^{-6D_r t}\right)$$

Substitution of this result in the equation of the motion of $< \hat{u}_3^2\, \hat{u}_1^2 >$ gives

$$\begin{aligned}\frac{d}{dt}\left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle &= D_r \left[-20\left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle + 2\left(1 - \left\langle \hat{u}_2^2 \right\rangle\right)\right] \\ &= -20D_r \left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle + \frac{4}{3} D_r \left(1 + \frac{1}{2} e^{-6D_r t}\right)\end{aligned}$$

Again, first the homogeneous equation is solved

$$\frac{d}{dt}\left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle = -20D_r \left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle$$

which gives

$$\left\langle \hat{u}_3^2 \hat{u}_1^2 \right\rangle = B\, e^{-20D_r t}$$

The integration constant is again considered now a function of time such that it satisfies the full equation of motion. Substitution into the equation of motion leads to

$$\frac{d}{dt}B(t) = \frac{4}{3}D_r\left(1+\frac{1}{2}e^{-6D_r t}\right)e^{+20D_r t} = \frac{4}{3}D_r e^{+20D_r t} + \frac{2}{3}D_r e^{+14D_r t}$$

and thus

$$\begin{aligned} B(t) &= B_0 + \frac{4}{3}D_r\frac{1}{20D_r}\left(e^{+20D_r t}-1\right)+\frac{2}{3}D_r\frac{1}{14D_r}\left(e^{+14D_r t}-1\right) \\ &= B_0 + \frac{1}{15}\left(e^{+20D_r t}-1\right)+\frac{1}{21}\left(e^{+14D_r t}-1\right) \\ &= B_0 + \frac{1}{15}e^{+20D_r t}+\frac{1}{21}e^{+14D_r t}-\left(\frac{1}{15}+\frac{1}{21}\right) \\ &= B_0 + \frac{1}{15}e^{+20D_r t}+\frac{1}{21}e^{+14D_r t}-\left(\frac{4}{35}\right) \end{aligned}$$

Since $B(t=0) \equiv B_0 = 0$, this reduces to

$$B(t) = \frac{1}{15}e^{+20D_r t}+\frac{1}{21}e^{+14D_r t}-\left(\frac{4}{35}\right)$$

We thus arrive at

$$\left\langle \hat{u}_3^2\hat{u}_1^2\right\rangle = \frac{1}{15}+\frac{1}{21}e^{-6D_r t}-\frac{4}{35}e^{-20D_r t}$$

This concludes the mathematical details in the derivation of the time dependence of the scattered intensity.

Exercises Chapter 5: HYDRODYNAMICS

San Francisco, CA, USA

5.4 The effective viscosity

On a length scale that is large in comparison to the size of the Brownian particles, a flowing suspension can be described as an "effective fluid" (see the figure). The Navier-Stokes on such a coarsened length scale is that of a mono-component fluid, where the viscosity is an "effective viscosity". The stress tensor is thus written as

$$\sum^{eff}(\vec{r}) = \eta^{eff}\left\{\nabla\vec{U}(\vec{r}) + \left(\nabla\vec{U}(\vec{r})\right)^{T}\right\} - P(\vec{r})\,\hat{I}$$

where $\vec{U}$ is the coarse-grained suspension velocity and P the pressure.

The effective viscosity η^{eff} depends on the volume fraction of colloids and the type of inter-colloidal interactions. In the present exercise we calculate the effective viscosity to leading order in concentration.

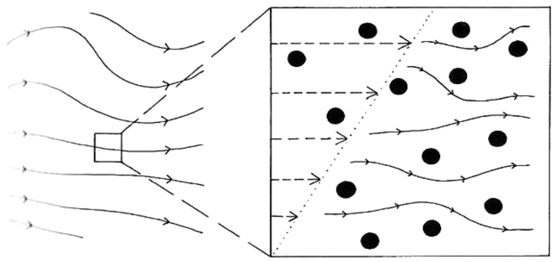


Fig. 5.10: Left: The flowing suspension on a length scale large compared to the size of a Brownian particle. Right: A blow up of a fictitious volume element, showing the flow on a length scale smaller than the size of the Brownian particles. The dotted straight line indicates the flow velocity gradient pertaining to the effective flow.

For non-interacting Brownian particles, the stress tensor at position $\vec{r}\,'$ is equal to

$$\sum\left(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N\left|\vec{r}\,'\right.\right)=\sum_{j=1}^{n}\Sigma_0\left(\vec{r}_j\left|\vec{r}\,'\right.\right)$$

where $\vec{r}_j$ is the position coordinate of colloidal particle j, and $\Sigma_0\left(\vec{r}_j\left|\vec{r}\,'\right.\right)$ is the stress generated by a single Brownian particle. For non-interacting colloids, the coarse-grained stress tensor is equal to

$$\sum{}^{eff}(\vec{r})=\frac{N}{V}\int_V d\vec{r}\,'\sum{}_0(\vec{r}\,')$$

The stress tensor *within the solvent* is equal to

$$\Sigma_0(\vec{r})=\eta_0\left\{\nabla\vec{u}_0(\vec{r}\,')+\left(\nabla\vec{u}_0(\vec{r}\,')\right)^T\right\}-p_0\left(\vec{r}\,'\right)\hat{I}$$

Here, $\vec{u}_0$ and p_0 are the solvent velocity and pressure on the small length scale, much smaller than the size of the colloidal spheres. At this point, we have to make the distinction between volume elements within the solvent and the core. Let V_0 denote the volume occupied by a single colloidal sphere with its center at the origin. The effective stress tensor is now written as

$$\sum{}^{eff}(\vec{r})=\frac{N}{V}\left\{\int_{V_0} d\vec{r}\,'\sum{}_0(\vec{r}\,')+\int_{V\backslash V_0} d\vec{r}\,'\sum{}_0(\vec{r}\,')\right\}$$

The volume $V \setminus V_0$ is occupied by solvent, for which the above formula for the stress tensor is valid. The integral over the volume V_0 occupied by the core can be cast into an integral over the surface area of the core, just inside the solvent. To this end we use the mathematical identity (summation over n is understood)

$$\Sigma_{0,ij}(\vec{r}\,') = \nabla_n{}'\left(\Sigma_{0,nj}(\vec{r}\,')r_i{}'\right) - \left(\nabla_n{}'\Sigma_{0,nj}(\vec{r}\,')\right)r_i{}'$$

From Gauss's integral theorem we thus have (with ∂V_0 the surface of V_0)

$$\int_{V_0} d\vec{r}\,'\Sigma_{0,ij}(\vec{r}\,') = \oint_{\partial V_0} dS_n{}'\left(\Sigma_{0,nj}(\vec{r}\,')r_i{}'\right) - \int_{V_0} d\vec{r}\,'\left(\nabla_n{}'\Sigma_{0,nj}(\vec{r}\,')\right)r_i{}'$$

The body force $\nabla_n{}'\Sigma_{0,nj}$ is zero in a stationary state, or more generally, on a time scale that is large to the elastic relaxation time of the material of the colloidal core. The last integral therefore vanishes, so that, apart from pressure contributions

$$\sum\nolimits_{ij}^{eff}(\vec{r}) = \frac{N}{V}\left\{\oint_{\partial V_0} dS_n{}'\left(\Sigma_{0,nj}(\vec{r}\,')r_i{}'\right) + \int_{V\setminus V_0} d\vec{r}\,'\Sigma_{0,ij}(\vec{r}\,')\right\}$$

$$= \frac{N}{V}\left\{\oint_{\partial V_0} dS_n{}'\left(\Sigma_{0,nj}(\vec{r}\,')r_i{}'\right) + \eta_0 \int_{V\setminus V_0} d\vec{r}\,'\left\{\nabla_i\,\vec{u}_{0,j}(\vec{r}\,') + \left(\nabla_i\,\vec{u}_{0,j}(\vec{r}\,')\right)^T\right\}\right\}$$

The coarse-grained values of gradients of the suspension velocity $\vec{U}$ are, similarly to the coarse-grained stress tensor, defined as a spatial average of the corresponding microscopic flow velocity $\vec{u}$

$$\left\{\nabla\vec{U}(\vec{r}\,') + \left(\nabla\vec{U}(\vec{r}\,')\right)^T\right\} \equiv \frac{N}{V}\int_V d\vec{r}\,'\left\{\nabla\vec{u}(\vec{r}\,') + \left(\nabla\vec{u}(\vec{r}\,')\right)^T\right\}$$

$$= \frac{N}{V}\left\{\int_{V\setminus V_0} d\vec{r}\,'\left\{\nabla\vec{u}_0(\vec{r}\,') + \left(\nabla\vec{u}_0(\vec{r}\,')\right)^T\right\} + \int_{V_0} d\vec{r}\,'\left\{\nabla\vec{u}(\vec{r}\,') + \left(\nabla\vec{u}(\vec{r}\,')\right)^T\right\}\right\}$$

As before, $\vec{u}_0$ is the solvent velocity. Hence

$$\sum\nolimits^{eff}(\vec{r},t) = \eta_0\left\{\nabla U(\vec{r},t) + \left(\nabla U(\vec{r},t)\right)^T\right\} + \frac{N}{V}\oint_{\partial V_0} dS'\left(\hat{n}'\cdot\sum\nolimits_0(\vec{r}\,')r'\right)^T$$

$$-\eta_0\frac{N}{V}\int_{V_0} d\vec{r}\,'\left\{\nabla'\vec{u}_0(\vec{r}\,') + \left(\nabla'\vec{u}_0(\vec{r}\,')\right)^T\right\}$$

where $\hat{n}$ is the unit normal vector pointing out of V_0 .

By Gauss's theorem

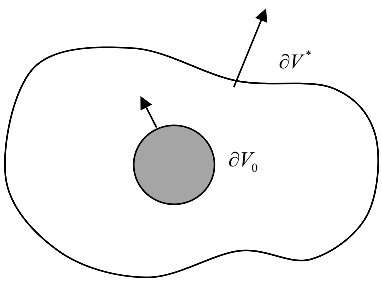
$$\int_{V_0} d\vec{r}\,'\nabla_i\,\vec{u}_j(\vec{r}\,') = \oint_{\partial V_0} d\vec{S}_i\,'\vec{u}_{0,j}(\vec{r}\,')$$

so that the above expression can be rewritten as

$$\sum\nolimits^{eff}(\vec{r},t) = \eta_0\left\{\nabla U(\vec{r},t) + \left(\nabla U(\vec{r},t)\right)^T\right\}$$
$$+\frac{N}{V}\oint_{\partial V_0} dS\,'\left\{\vec{r}\,'\left(\sum\nolimits_0(\vec{r}\,')\cdot\hat{n}\,'\right) - \eta_0\left(\hat{n}\,'\vec{u}_0(\vec{r}\,') + \vec{u}_0(\vec{r}\,')\,\hat{n}\,'\right)\right\}$$

Let V^* be an arbitrary larger volume that contains V_0 (see the figure), and consider

$$\left(\oint_{\partial V^*} - \oint_{\partial V_0}\right) dS\,'\left\{\vec{r}\,'\left(\hat{n}\,'\cdot\Sigma_0(\vec{r}\,')\right) - \eta_0\left\{\hat{n}\,'\vec{u}_0(\vec{r}\,') + \vec{u}_0\hat{n}\,'(\vec{r}\,')\right\}\right\}$$



The normal vectors are always assumed to point outwards the volumes. According to Gauss' integral theorem, this integral is equal to

$$\int_{V^*\setminus V_0} d\vec{r}\,'\left\{\vec{r}\,'\left(\nabla\,'\cdot\Sigma_0(\vec{r}\,')\right) + \Sigma_0(\vec{r}\,') - \eta_0\left\{\nabla\,'\vec{u}_0(\vec{r}\,') + (\nabla\,'\vec{u}_0(\vec{r}\,'))^T\right\}\right\}$$

Since, as before, $\nabla\,'\cdot\Sigma_0(\vec{r}\,') = 0$, and the stress tensor drops against the last terms (apart from pressure contributions), the integral is thus zero. This implies that we can use, instead of ∂V_0 , any surface area ∂V^* that encloses V_0 . Hence

$$\sum\nolimits^{eff}(\vec{r},t) = \eta_0\left\{\nabla U(\vec{r},t) + \left(\nabla U(\vec{r},t)\right)^T\right\}$$
$$+\frac{N}{V}\oint_{\partial V^*} dS\,'\left\{\vec{r}\,'\left(\sum\nolimits_0(\vec{r}\,')\cdot\hat{n}\,'\right) - \eta_0\left(\hat{n}\,'\vec{u}_0(\vec{r}\,') + \vec{u}_0(\vec{r}\,')\,\hat{n}\,'\right)\right\}$$

Without loss of the generality, we can take ∂V^* as a spherical surface with an arbitrary large radius and with the colloidal sphere at the origin.

Since the force on a single, non-interacting sphere is zero, it follows from eqn. (5.109) that

$$\vec{u}_0(\vec{r}) = -\frac{5}{2}\left(\left(\frac{a}{r}\right)^3 - \left(\frac{a}{r}\right)^5\right)\left(\frac{\vec{r}}{r}\cdot\ddot{E}\cdot\frac{\vec{r}}{r}\right)\vec{r} - \left(\frac{a}{r}\right)^5 \ddot{E}\cdot\vec{r}$$

where $\ddot{E}$ is the symmetric part of the velocity-gradient tensor

$$\ddot{E} = \frac{1}{2}\left\{\nabla\vec{U}(\vec{r}\,') + \left(\nabla\vec{U}(\vec{r}\,')\right)^T\right\}$$

Since ∂V^* is the surface area of a sphere with arbitrary large radius R, the surface area of which varies like R^2, all terms in this expression for the solvent flow velocity that vanish faster than r^{-2} can be neglected. The relevant expression is therefore

$$\vec{u}_0(\vec{r}) = -\frac{5}{2}\left(\frac{a}{r}\right)^3\left(\frac{\vec{r}}{r}\cdot\ddot{E}\cdot\frac{\vec{r}}{r}\right)\vec{r}$$

It follows that (again not denoting irrelevant terms)

$$\begin{aligned}\nabla_i\,\vec{u}_{0,j}(\vec{r}) &= -\frac{5}{2}\ddot{E}_{nm}\,a^3\,\nabla_i\left(\frac{r_n\,r_m\,r_j}{r^5}\right)\\ &= -\frac{5}{2}E_{nm}\frac{a^3}{r^5}\left(\delta_{ni}\,r_m\,r_j + \delta_{mi}\,r_n\,r_j + \delta_{nm}\,r_i\,r_j - 5\frac{r_n\,r_m\,r_i\,r_j}{r^2}\right)\end{aligned}$$

which leads to

$$\Sigma_0(\vec{r}) = -5\,\eta_0\frac{a^3}{r^3}\left(\left(\ddot{E}\cdot\hat{n}\right)\hat{n} + \hat{n}\left(\ddot{E}\cdot\hat{n}\right) - 5\,\hat{n}\,\hat{n}\left(\hat{n}\cdot\ddot{E}\cdot\hat{n}\right)\right)$$

where it is used that $\ddot{E}$ is traceless ($Tr\left(\ddot{E}\right) = E_{nm}\,\delta_{nm} = 0$). The effective stress tensor is thus found to be equal to

$$\begin{aligned}\sum{}^{eff}(\vec{r}) &= \eta_0\left\{\nabla\vec{U}(\vec{r}\,') + \left(\nabla\vec{U}(\vec{r}\,')\right)^T\right\}\\ &\quad + 5\frac{N}{V}\eta_0\,a^3\oint dn'\,\left(5\,\hat{n}'\,\hat{n}'\left(\hat{n}'\bullet\ddot{E}\bullet\hat{n}'\right) - \hat{n}'\left(\hat{n}'\bullet\ddot{E}\right)\right)\end{aligned}$$

where the integral now ranges over the unit spherical surface (the spherical surface with unit radius). The angular integrations are evaluated, using that

$$\oint d\hat{n}'\hat{n}_i'\hat{n}_j'\hat{n}_p'\hat{n}_q' = \frac{4\pi}{15}\left[\delta_{ij}\delta_{pq} + \delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}\right]$$
$$\oint d\hat{n}'\hat{n}_i'\hat{n}_p' = \frac{4\pi}{3}\delta_{ip}$$

The final result is

$$\sum^{eff}(\vec{r}) = \eta_0\left(1 + \frac{5}{2}\frac{N}{V}\frac{4\pi}{3}a^3\right)\left\{\nabla\vec{U}(\vec{r}\,') + \left(\nabla\vec{U}(\vec{r}\,')\right)^T\right\}$$

so that the effective viscosity is equal to

$$\eta^{eff} = \eta_0\left(1 + \frac{5}{2}\frac{N}{V}\frac{4\pi}{3}a^3\right) = \eta_0\left(1 + \frac{5}{2}\phi\right)$$

In the last equation we introduced the volume fraction of colloids

$$\phi = \frac{N}{V}\frac{4\pi}{3}a^3$$

There are two things to be noted about the above derivation:

- This formula is only valid for low concentrations, where inter-colloidal interactions are not important. In this case of non-interacting colloids, the mere presence of the core induces an additional stress that is proportional to the number of colloids. Interactions determine the second order in volume fraction dependence of the viscosity.
-It is also assumed that the core of the spherical colloid is not deformed by the applied shear forces, or by any other external field. An additional external field that exerts a torque on the sphere in-validates the above expression for the effective viscosity. In using eqn. (5.109) is has been assumed that the sphere is torque-free. In the presence of an external field that acts with a torque on the colloids, eqn. (5.109) must first be extended to a non-zero torque.

5.5 Oseen's approximation for hydrodynamic interactions

For point-like Brownian particles, the hydrodynamic force density is concentrated at the origin of the spheres

$$\vec{f}^{ext}(\vec{r}\,') = -\sum_{j=1}^{N} \vec{F}_j^h\, \delta\left(\vec{r}\,' - \vec{r}_j\right)$$

Let us start with the fluid flow velocity that is equal to

$$\begin{aligned}\vec{u}(\vec{r}) &= \int d\vec{r}\,'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}^{ext}(\vec{r}\,') \\ &= \sum_{j=1}^{N} \int d\vec{r}\,'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_j(\vec{r}\,')\end{aligned}$$

where $\vec{f}_j$ is the force per unit area that surface elements of particle *j* exert on the solvent.

For $\vec{r} = \vec{r}_i$ the above formula leads to divergence problems in case *j=i* when the delta-representation in the first equation for point particles is directly substituted. We therefore isolate the term for *j=i* from the sum

$$\vec{u}(\vec{r}) = \int d\vec{r}\,'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_i(\vec{r}\,') + \sum_{j \neq i} \int d\vec{r}\,'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_j(\vec{r}\,')$$

In the sum we can substitute the very first formula, omitting the term for *j=i*

$$\sum_{j \neq i} \int d\vec{r}\,'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_j(\vec{r}\,') = -\sum_{j \neq i} \vec{T}\left(\vec{r} - \vec{r}_j\right) \cdot \vec{F}_j^h$$

The first integral in the above equation is rewritten in terms of a surface integral

$$\vec{u}(\vec{r}) = \oint_{\partial V_i} dS'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_i(\vec{r}\,') - \sum_{j \neq i} \vec{T}\left(\vec{r} - \vec{r}_J\right) \cdot \vec{F}_j^h$$

where now $\vec{f}_i(\vec{r})$ is the force per unit area which surface elements of particle *i* exert on the solvent. As shown that in appendix A (in Jan's book)

$$\boxed{\oint_{\partial V_i} dS'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) = \hat{I}\, \frac{2a}{3\eta_o}, \quad for\ \vec{r} \in \partial V_i}$$

Now operate on both sides of the above expression for the flow velocity with the operator

$$\frac{1}{4\pi a^2} \oint_{\partial V_i} dS\,(\cdots)$$

According to the above mathematical identity we have

$$\frac{1}{4\pi a^2} \oint_{\partial V_i} dS \oint_{\partial V_i} dS'\, \vec{T}\left(\vec{r} - \vec{r}\,'\right) \cdot \vec{f}_j(\vec{r}\,') = -\frac{1}{6\pi\eta_0 a} \vec{F}_i^h,$$

Since for stick boundary conditions we have

$$\vec{u}(\vec{r}) = \vec{v}_i + \vec{\Omega}_i \times \left(\vec{r} - \vec{r}_i\right), \qquad \vec{r} \in \partial V_i$$

the same integration of the velocity gives

$$\frac{1}{4\pi a^2} \oint_{\partial V_i} dS\, \vec{u}(\vec{r}) = \vec{v}_i$$

We thus arrive at

$$\vec{v}_i = -\frac{1}{6\pi\eta_0 a} \vec{F}_i^h - \sum_{j \neq i}^{N} \vec{T}\left(\vec{r} - \vec{r}_j\right) \cdot \vec{F}_j^h$$

which can be rewritten as

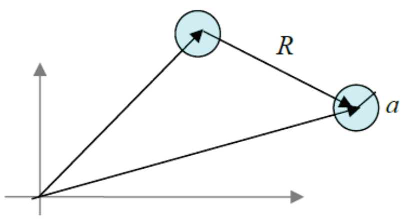
$$\vec{v}_i \equiv -\beta \sum_{j=1}^{N} \vec{D}_{ij} \cdot \vec{F}_j^h$$

with

$$\boxed{\begin{aligned} \vec{D}_{ii} &= \frac{k_B T}{6\pi\eta_0 a} \hat{I} = D_0\, \hat{I} \\ \vec{D}_{ij} &= k_B T\, \vec{T}\left(\vec{r}_i - \vec{r}_j\right) = \frac{3}{4} D_0 \frac{a}{r_{ij}} \left(\hat{I} + \hat{r}_{ij}\, \hat{r}_{ij}\right), \quad i \neq j \end{aligned}}$$

where it is used that the Oseen tensor is equal to

$$\vec{T}\left(\vec{r}\right) = -\frac{1}{8\pi\eta_0 a} \left(\hat{I} + \frac{\vec{r}\,\vec{r}}{r^2}\right)$$



This is a good approximation for hydrodynamics interactions when the distance R between the spheres is much larger than their radius a (as sketched in the above figure).

5.6 Sedimentation of two spheres

Consider two spheres in a fluid, which are subjected to a gravitational force that is equal for both spheres. We consider in this exercise the stationary velocities that the spheres attain. The velocities of the two spheres are equal to

$$\vec{v}_1 = -\beta\vec{\vec{D}}_{11}\cdot\vec{F}_1^h - \beta\vec{\vec{D}}_{12}\cdot\vec{F}_2^h$$
$$\vec{v}_2 = -\beta\vec{\vec{D}}_{21}\cdot\vec{F}_1^h - \beta\vec{\vec{D}}_{22}\cdot\vec{F}_2^h$$

where $\vec{F}_j^h$ is the hydrodynamic force on sphere j. In the stationary state the total force on the spheres is zero, so that the gravitational external force $\vec{F}_j^h$ is equal but opposite in sign to both $\vec{F}^{ext}$

$$\vec{F}_j^h + \vec{F}^{ext} = \vec{0} \quad (j = 1, 2) \quad \vec{F}^{ext} = m\vec{g}$$

Hence

$$\vec{v}_1 = \beta\left[\vec{\vec{D}}_{11}(\vec{r}_{12}) + \vec{\vec{D}}_{12}(\vec{r}_{12})\right]\cdot\vec{F}^{ext}$$
$$\vec{v}_2 = \beta\left[\vec{\vec{D}}_{21}(\vec{r}_{21}) + \vec{\vec{D}}_{22}(\vec{r}_{21})\right]\cdot\vec{F}^{ext}$$

Since

$$\vec{\vec{D}}_{11}(\vec{r}_{12}) = \vec{\vec{D}}_{11}(-\vec{r}_{21})$$

$$\vec{\vec{D}}_{12}(-\vec{r}_{12}) = \vec{\vec{D}}_{12}(\vec{r}_{21}) = \vec{\vec{D}}_{21}(\vec{r}_{21})$$

it follows that the velocities of the two spheres are the same: $\vec{v} \equiv \vec{v}_1 = \vec{v}_2$

Within the Oseen approximation for the hydrodynamic interaction functions we have

$$\vec{\vec{D}}_{11} = \vec{\vec{D}}_{22} = \frac{k_B T}{6\pi\eta_0 a}\hat{I} \equiv D_0\,\hat{I}$$
$$\vec{\vec{D}}_{12} = \vec{\vec{D}}_{21} = k_B T\,\vec{\vec{T}}(\vec{r}_{12}) = \frac{3}{4}D_0\frac{a}{r_{12}}\left(\hat{I} + \hat{r}_{12}\,\hat{r}_{12}\right),$$

The velocity is then given by

$$\boxed{\vec{v} = \beta D_0\left[\left(1 + \frac{3}{4}\frac{a}{r_{12}}\right)\hat{I} + \frac{3}{4}\frac{a}{r_{12}}\hat{r}_{12}\,\hat{r}_{12}\right]\cdot\vec{F}^{ext}}$$

This expression can be inverted in order to express the force in terms of the velocity. We have to invert a tensor of the form $\vec{\vec{M}} \equiv C_1\,\hat{I} + C_2\,\hat{r}\,\hat{r}$.

Use the following Ansatz for the inverse tensor

$$\vec{\vec{M}}^{-1} \equiv D_1 \,\hat{I} + D_2 \,\hat{r}\,\hat{r}$$

Now use that $(\hat{r}\,\hat{r})\cdot(\hat{r}\,\hat{r}) = \hat{r}\left(\hat{r}\cdot\hat{r}\right)\hat{r} = \hat{r}\,\hat{r}$ to evaluate

$$\vec{\vec{M}}\cdot\vec{\vec{M}}^{-1} = \hat{I} = C_1 D_1 \,\hat{I} + \left[C_1 D_2 + C_2 D_1 + C_2 D_2 \right]\hat{r}\,\hat{r}$$

so that

$$C_1 D_1 = 1$$
$$\left[C_1 D_2 + C_2 D_1 + C_2 D_2 \right] = 0$$

Thus

$$D_1 = \frac{1}{C_1} \quad and \quad D_2 = -\frac{C_2}{C_1}\frac{1}{C_1 + C_2}$$

In our case

$$C_1 = \beta D_0 \left(1 + \frac{3}{4}\frac{a}{r_{12}}\right)$$

$$C_2 = \beta D_0 \frac{3}{4}\frac{a}{r_{12}}$$

so that, to leading order in a/r_{12}

$$D_1 = \frac{1}{\beta D_0 \left(1 + \frac{3}{4}\frac{a}{r_{12}}\right)} \approx \frac{1}{\beta D_0}\left(1 - \frac{3}{4}\frac{a}{r_{12}}\right)$$

$$D_2 = -\frac{\beta D_0 \frac{3}{4}\frac{a}{r_{12}}}{\beta D_0 \left(1 + \frac{3}{4}\frac{a}{r_{12}}\right)} \frac{1}{\beta D_0 \left(1 + \frac{3}{2}\frac{a}{r_{12}}\right)} \approx -\frac{1}{\beta D_0}\frac{3}{4}\frac{a}{r_{12}}\left(1 - \frac{3}{4}\frac{a}{r_{12}}\right)\left(1 - \frac{3}{2}\frac{a}{r_{12}}\right)$$
$$\approx -\frac{1}{\beta D_0}\frac{3}{4}\frac{a}{r_{12}}$$

Using that $\beta D_0 = 1/6\pi\eta_0 a$, we thus find

$$\boxed{\vec{F}^{ext} = 6\pi\eta_0 a\left[\left(1 - \frac{3}{4}\frac{a}{r_{12}}\right)\hat{I} - \frac{3}{4}\frac{a}{r_{12}}\hat{r}_{12}\,\hat{r}_{12}\right]\cdot\vec{v}}$$

Consider now two particular configurations of the two particles:

(a) $\hat{r}_{12}$ and $\vec{v}$ are co-linear (see figure (a) below). In that case

$$\hat{r}_{12}\,\hat{r}_{12}\cdot\vec{v} = \hat{r}_{12}\,|\vec{v}| = \vec{v}$$

and hence

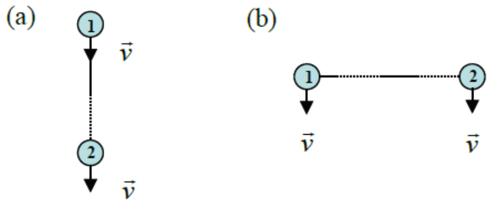
$$\vec{F}^{ext} = 6\pi\eta_0 a\left[1-\frac{3}{2}\frac{a}{r_{12}}\right]\vec{v}$$

The velocity is thus co-linear with the gravitational force, and the friction coefficient is less than $6\pi\eta_0 a$, so that the spheres sediment faster than a single sphere for a given external force field.

(b) $\hat{r}_{12}$ and $\vec{v}$ are perpendicular (see figure (b) below), so that $\hat{r}_{12}\cdot\vec{v}=0$
The force is now equal to

$$\vec{F}^{ext} = 6\pi\eta_0 a\left(1-\frac{3}{4}\frac{a}{r_{12}}\right)\vec{v}$$

Again the spheres sediment faster than the single sphere, in the absence of other spheres.



In fact, since $|\hat{r}_{12}\,\hat{r}_{12}\cdot\vec{v}| = |\hat{r}_{12}\cdot\vec{v}| = |\vec{v}|\cos\theta \le |\vec{v}|$, where θ is the smallest angle between $\hat{r}_{12}$ and $\vec{v}$, the friction coefficient is smaller than $6\pi\eta_0 a$ for all configurations.

Note that the force balance equation used here assumes that the two spheres are at a sufficiently large distance, such that direct interactions (through a potential, for example due to surface charges) are absent.

5.8 Hydrodynamic interaction of two unequal spheres

Consider two spheres, i and j, with unequal radii a_i and a_j, respectively. Let us discuss the first few terms in the reciprocal distance expansion of hydrodynamic interaction matrices.

(a) We will show that the Rodne-Prager matrix is given by

$$\vec{D}_{ij} = \frac{k_B T}{6\pi\eta_0 a} \frac{a_j}{r_{ij}} \left\{ \frac{3}{4}\left[\hat{I} + \hat{r}_{ij}\hat{r}_{ij} \right] + \frac{1}{4} \frac{a_i^2 + a_j^2}{r_{ij}^{\;2}} \left[\hat{I} - 3\hat{r}_{ij}\hat{r}_{ij} \right] \right\}$$

Everything that is done in the book is concerned with equally sized particles. Here two particles (i and j) are considered with different radii a_i and a_j ($a_j \neq a_i$). Let $\vec{v}_i$ be the velocity of particle of i. It induces a velocity field, in the absence of particle j, according to eqn. (5.36)

$$\vec{u}_0\left(\vec{r}\right) = \left\{ \frac{3}{4} \frac{a_i}{\left|\vec{r} - \vec{r}_i\right|} \left[\hat{I} + \frac{\left(\vec{r} - \vec{r}_i\right)\left(\vec{r} - \vec{r}_i\right)}{\left|\vec{r} - \vec{r}_i\right|^2} \right] + \frac{1}{4} \left(\frac{a_i}{\left|\vec{r} - \vec{r}_i\right|} \right)^3 \left[\hat{I} - 3\frac{\left(\vec{r} - \vec{r}_i\right)\left(\vec{r} - \vec{r}_i\right)}{\left|\vec{r} - \vec{r}_i\right|^2} \right] \right\} \cdot \vec{v}_i$$

where $\vec{r}_i$ is the position coordinate of sphere i. The velocity of sphere j that is at the position of $\vec{r}_j$, is according to Faxen's theorem, eqn. (5.60)

$$\vec{v}_j = -\frac{1}{6\pi\eta_0 a_j} \vec{F}_j^h + \vec{u}_0\left(\vec{r}_j\right) + \frac{1}{6} a_j^2 \nabla_j^2 \vec{u}_0\left(\vec{r}_j\right)$$

where ∇_j is the gradient operator with respect to $\vec{r}_j$. Using the identities

$$\nabla^2 \left(\frac{1}{r^n} \right) = \frac{n^2 - n}{r^{n+2}},$$

$$\nabla^2 \left(\frac{\vec{r}\,\vec{r}}{r^m} \right) = \frac{2}{r^m} \hat{I} + \frac{\vec{r}\,\vec{r}}{r^{m+2}} \left(m^2 - 5m \right)$$

it is readily found that

$$\nabla_j^2 \vec{u}_0\left(\vec{r}_j\right) = \frac{3}{2} \frac{a_i}{r_{ij}^3} \left(\hat{I} - 3\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^2} \right) \cdot \vec{v}_i$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$.

Hence

$$\vec{v}_j = -\frac{1}{6\pi\eta_0 a_j}\vec{F}_j^h + \frac{3}{2}\frac{a_i}{r_{ij}}\left\{\left(\frac{1}{2}+\frac{1}{6}\frac{a_i^2+a_j^2}{r_{ij}^2}\right)\hat{I} + \frac{1}{2}\left(1-\frac{a_i^2+a_j^2}{r_{ij}^2}\right)\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^2}\right\}\cdot\vec{v}_i$$

Within this zeroth order reflection

$$\vec{v}_i = -\frac{1}{6\pi\eta_0 a_i}\vec{F}_i^h$$

so that it is found that

with

$$\vec{v}_j = -\frac{1}{6\pi\eta_0 a_j}\vec{F}_j^h - \beta\,\vec{D}_{ji}\cdot\vec{F}_i^h$$

$$\boxed{\vec{D}_{ji} = \frac{k_B T}{6\pi\eta_0 a_i}\frac{3}{2}\frac{a_i}{r_{ij}}\left\{\left(\frac{1}{2}+\frac{1}{6}\frac{a_i^2+a_j^2}{r_{ij}^2}\right)\hat{I} + \frac{1}{2}\left(1-\frac{a_i^2+a_j^2}{r_{ij}^2}\right)\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^2}\right\}}$$

(b) The flow field of sphere i is reflected by sphere j. The reflected flow field $\vec{u}^{(1)}(\vec{r})$ from sphere j back to sphere i is, according to eqn.(5.92), equal to

$$\begin{aligned}
\vec{u}^{(1)}(\vec{r}) &= \vec{U}^{(2)}(\vec{r}-\vec{r}_j)\odot\left[\vec{v}_j^{(1)} - \vec{u}^{(0)}(\vec{r}_j)\right] \\
&-\frac{1}{2}\vec{U}^{(3)}(\vec{r}-\vec{r}_j)\odot\left[\nabla_j\vec{u}^{(0)}(\vec{r}_j) + \left(\nabla_j\vec{u}^{(0)}(\vec{r}_j)\right)^T\right] \\
&-\frac{1}{2}\vec{U}^{(4)}(\vec{r}-\vec{r}_j)\odot\left[\nabla_j\nabla_j\vec{u}^{(0)}(\vec{r}_j)\right] \\
&-\frac{1}{6}\vec{U}^{(5)}(\vec{r}-\vec{r}_j)\odot\left[\nabla_j\nabla_j\nabla_j\vec{u}^{(0)}(\vec{r}_j)\right] + \cdots
\end{aligned}$$

where

$$\vec{u}^{(0)}(\vec{r}) = \vec{U}_{a_i}^{(2)}(\vec{r}-\vec{r}_i)\odot(-\vec{v}_i) = \vec{U}_{a_i}^{(2)}(\vec{r}-\vec{r}_i)\odot\left(\frac{1}{6\pi\eta_0 a}\vec{F}_i^h\right)$$

is the flow field that originates from the moving sphere i in an otherwise quiescent solvent. In the present case, $\vec{u}_0(\vec{r})$ in eqn.(5.80) for the calculation of $\vec{u}_0(\vec{r})$, is equal to $-\vec{v}_i$ (a moving sphere in an otherwise quiescent solvent is equivalent to a sphere at the origin in a solvent that uniformly flows in the opposite direction). Eqn.(5.80) then predicts the resulting flow velocity induced by the sphere when it is inserted at the origin in the uniformly flowing solvent.

Since the velocity of the sphere is equal to $-\vec{F}_i^h / 6\pi\eta_0 a$, eqn. (5.80) gives the above given expression for $\vec{u}^{(0)}(\vec{r})$. Explicit evaluation of this expression, using the first entry in table 5.1 and the defining expression

$$H^{(n)} = (\nabla)^n \frac{1}{r}$$

leads to the given expression for $\vec{u}_0(\vec{r})$ in (a), as it should.

Next consider the evaluation of $\vec{u}^{(1)}(\vec{r})$. We are only interested in the leading order expansion with respect to a / r_{ij}, so that only the leading order contributions of the connectors need to be considered.

Since $H^{(m)}(\vec{r}) \sim r^{-(m+1)}$, it follows from table 5.1 on page 265 and the table 5.2 on page 299 that, up to leading order (note that is Faxen's theorem $\vec{r}$ will be taken equal to $\vec{r}_i$):

$$\vec{U}^{(2)}\left(\vec{r}-\vec{r}_j\right) \to \frac{a_j}{4} R^2 \nabla\nabla \frac{1}{R} + a_j \hat{I} \frac{1}{R}$$

$$\vec{U}^{(3)}\left(\vec{r}-\vec{r}_j\right) \to -\frac{a_j^3}{6} R^2 \nabla\nabla\nabla \frac{1}{R} - a_j^{\,3} \hat{I} \nabla \frac{1}{R}$$

$$\vec{U}^{(4)}\left(\vec{r}-\vec{r}_j\right) \to \frac{a_j^{\,5}}{12} R^2 \nabla\nabla \frac{1}{R} \hat{I} + \frac{a_j^{\,5}}{3} \hat{I} \frac{1}{R} \hat{I}$$

$$\vec{U}^{(5)}\left(\vec{r}-\vec{r}_j\right) \to -\frac{9a_j^{\,3}}{6*5!!} R^2 \, \nabla\nabla\nabla \frac{1}{R} \hat{I} - \frac{9a_j^{\,5}}{5!!} \hat{I} \nabla \frac{1}{R} \hat{I}$$

where $\vec{R} \equiv \vec{r} - \vec{r}_j$. As can be seen from the table 5.1, the remaining terms are of higher order, and can therefore be omitted. Also, to leading order (see (a))

$$\vec{u}^{(0)}\left(\vec{r}\right) = \frac{3}{4} \frac{a_j}{\left|\vec{r} - \vec{r}_j\right|} \left[\hat{I} + \frac{\left(\vec{r}-\vec{r}_j\right)\left(\vec{r}-\vec{r}_j\right)}{\left|\vec{r} - \vec{r}_j\right|^2} \right] \cdot \vec{v}_i^{(0)}$$

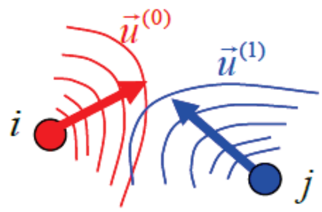
According to the equation that we had for $\vec{u}^{(1)}(\vec{r})$, we thus have to leading order in a_j / R

$$\vec{u}^{(1)}\left(\vec{r}\right) = \vec{U}^{(2)}(\vec{R}) \odot \left[\vec{v}_j^{(1)} - \vec{u}^{(0)}(\vec{r}_j) \right]$$

Now, according to the formula for $\vec{v}_j^{(1)}$ on page 259, again to leading order, this results in a zero (note that the force $\vec{F}_j^h$ in the formula on page 259 does not contribute to $\vec{D}_{ii}$, and can therefore be omitted here). Since the leading terms cancel, we have to resort to the next higher order terms $\sim (a_j / R)^2$.

Keeping the leading order terms in the connectors, and noting that

$$(\nabla_j)^n \vec{u}^{(0)}\left(\vec{r}_j\right) \sim (a_j / R)^{n+1}$$



we thus arrive at

$$\begin{aligned}\vec{u}_j^{(1)} &= \left[\frac{a_j}{4} R^2 \nabla\nabla \frac{1}{R} + a_j \hat{I} \frac{1}{R}\right] \odot \left[\frac{1}{6} a_j^2 \nabla_j^2 \vec{u}^{(0)}(\vec{r}_j)\right] \\ &+ \frac{1}{2}\left[\frac{a_j^3}{6} R^2 \nabla\nabla\nabla \frac{1}{R} + a_j^3 \hat{I} \nabla \frac{1}{R}\right] \odot \left[\nabla_j \vec{u}^{(0)}(\vec{r}_j) + (\nabla_j \vec{u}^{(0)}(\vec{r}_j))^T\right] \\ &- \frac{1}{2}\left[\frac{a_j^3}{12} R^2 \nabla\nabla \frac{1}{R} \hat{I} + \frac{a_j^3}{3} \hat{I} \frac{1}{R} \hat{I}\right] \odot \left[\nabla_j \nabla_j \vec{u}^{(0)}(\vec{r}_j)\right]\end{aligned}$$

where the first line corresponds to $\vec{U}^{(2)}$, the second line to $\vec{U}^{(3)}$ and the third to $\vec{U}^{(4)}$.

Since $\hat{I} : \nabla_j \nabla_j = \nabla_j^2$, the first term cancels against the last term.

Hence, to leading order we get

$$\begin{aligned}\vec{u}_j^{(1)}(\vec{r}) &= -\frac{1}{2} \vec{U}^{(3)}(\vec{R}) \odot \left[\nabla_j \vec{u}^{(0)}(\vec{r}_j) + (\nabla_j \vec{u}^{(0)}(\vec{r}_j))^T\right] \\ &= \frac{1}{2}\left[\frac{a_j^3}{6} R^2 \nabla\nabla\nabla \frac{1}{R} + a_j^3 \hat{I} \nabla \frac{1}{R}\right] \odot \left[\nabla_j \vec{u}^{(0)}(\vec{r}_j) + (\nabla_j \vec{u}^{(0)}(\vec{r}_j))^T\right]\end{aligned}$$

Using the identities

$$\nabla_i \frac{1}{r_{ij}} = -\frac{\vec{r}_{ij}}{r_{ij}^{\ 3}}$$

$$\nabla_{i\alpha} \nabla_{i\beta} \nabla_{i\gamma} \frac{1}{r_{ij}} = \frac{3}{r_{ij}^{\ 5}}\left(\delta_{\alpha\beta}\, r_{i\gamma} + \delta_{\alpha\gamma}\, r_{i\beta} + \delta_{\beta\gamma}\, r_{i\alpha}\right) - 15 \frac{r_{ij,\alpha}\, r_{ij,\beta}\, r_{ij,\gamma}}{r_{ij}^{\ 7}}$$

and

$$\left[\nabla_j \vec{u}^{(0)}\left(\vec{r}_j\right)+\left(\nabla_j \vec{u}^{(0)}\left(\vec{r}_j\right)\right)^T\right]=\frac{1}{4\pi\eta_0\, r_{ij}^{\;3}}\left[\hat{I}-3\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^{\;3}}\right]\left(\vec{r}_{ij}\cdot\vec{F}_i^h\right)$$

the velocity of sphere I resulting from the reflected flow field is found to be equal to (contraction with respect to β and γ is taken here)

$$\vec{v}_{i,\alpha}^{(2)}=\frac{1}{8\pi\eta_0\, r_{ij}^{\;3}}\sum_{\beta,\gamma}\left[\begin{array}{c}\frac{a_j^{\;3}}{6}\left(\frac{3}{r_{ij}^{\;3}}\right)\left(\delta_{\alpha\beta}\, r_{i\gamma}+\delta_{\alpha\gamma}\, r_{i\beta}+\delta_{\beta\gamma}\, r_{i\alpha}\right)\\ -15\frac{r_{ij,\alpha}\, r_{ij,\beta}\, r_{ij,\gamma}}{r_{ij}^{\;5}}-a_j^{\;3}\frac{r_\gamma}{r_{ij}^{\;3}}\end{array}\right]\left[\delta_{\alpha\beta}-3\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^{\;3}}\right]\left(\vec{r}_{ij}\cdot\vec{F}_i^h\right)$$

Keeping again only the leading order terms finally leads to

$$\vec{v}_j^{(2)}=\frac{a_j^{\;3}}{8\pi\eta_0}\frac{10}{6}\frac{\vec{r}_{ij}\,\vec{r}_{ij}}{r_{ij}^{\;6}}\cdot\vec{F}_i^h$$

Hence, by definition we find that

$$\boxed{\vec{\vec{D}}_{ij}=-\frac{k_B T}{6\pi\eta_0 a}\frac{15}{4}\frac{a_i a_j^3}{r_{ij}^4}\hat{r}_{ij}\hat{r}_{ij}}$$

5.9 Friction of a rod in shear flow

(a) Consider a rod with its center at the origin and with an angular velocity $\vec{\Omega}$. Similar arguments as for a rotating rod in a quiescent fluid can be used to show that the force on a bead i is proportional to its velocity relative to the local shear flow velocity $\vec{\Gamma}\cdot\vec{r}$.

The friction forces parallel and perpendicular to the rod axis are proportional to the velocity $\vec{\Omega}\times\vec{r}$ relative to the local shear flow velocity $\vec{\Gamma}\cdot\vec{r}$.

The force $\vec{F}^h_{j,\parallel}$ on bead *j* along the axis of rods is therefore

$$\vec{F}^h_{j,\parallel} = -C_\parallel\, \hat{u}\,\hat{u}\cdot\left[\vec{\Omega}\times\vec{r}_j - \vec{\Gamma}\cdot\vec{r}_j\right]$$

while the force perpendicular to the long axis is

$$\vec{F}^h_{j,\perp} = -C_\perp\left(\hat{I}-\hat{u}\,\hat{u}\right)\cdot\left[\vec{\Omega}\times\vec{r}_j - \vec{\Gamma}\cdot\vec{r}_j\right]$$

The problem now is to determine the constants $C_\parallel$ and $C_\perp$. Since for long and thin rods $\vec{r}_j = jD\hat{u}$, the total force is thus

$$\begin{aligned}\vec{F}^h_j &= \vec{F}^h_{j,\parallel} + \vec{F}^h_{j,\perp}\\ &= -C_\parallel\, jD\left(\hat{u}\,\hat{u}\right)\cdot\vec{\Gamma}\cdot\hat{u} - C_\perp\, jD\cdot\left[\vec{\Omega}\times\hat{u} - \left(\hat{I}-\hat{u}\,\hat{u}\right)\vec{\Gamma}\cdot\hat{u}\right]\end{aligned}$$

According to eqn.(5.116) we have

$$\vec{F}^h_j = -3\pi\eta_0 D\left[\vec{v}_j - \vec{\Gamma}\cdot\vec{r}_j\right] - 3\pi\eta_0 D\left[\vec{u}_0\left(\vec{r}_j\right) + \frac{1}{24}D^2\,\nabla_j^2\vec{u}_0\left(\vec{r}_j\right)\right]$$

where $\vec{u}_0\left(\vec{r}\right)$ is again the flow that is generated by the remaining beads, in the absence of bead *j*. Again, the first term is the Stokes friction contribution to the force in an otherwise quiescent solvent, and the second term is due to the field generated by the other beads. The same reasoning to arrive at eq. (5.119) now leads to

$$\begin{aligned}\vec{F}^h_j &= -3\pi\eta_0 D\left[\vec{v}_j - \vec{\Gamma}\cdot\vec{r}_j\right] + \frac{3}{8}\hat{u}\,\hat{u}\sum_{i\neq j}\left[\frac{2}{|i-j|} - \frac{1}{6}\frac{1}{|i-j|^3}\right]\cdot\vec{F}^h_i\\ &\quad + \frac{3}{8}\left(\hat{I}-\hat{u}\,\hat{u}\right)\cdot\sum_{i\neq j}\left[\frac{1}{|i-j|} - \frac{1}{12}\frac{1}{|i-j|^3}\right]\cdot\vec{F}^h_i\end{aligned}$$

Now the hydrodynamic torque is defined as

$$
\begin{aligned}
\tau^h &= \sum_j \vec{r}_j \times \vec{F}_j^h = \sum_j jD\,\hat{u} \times \vec{F}_j^h \\
&= -C_\perp \sum_j (jD)^2\,\hat{u} \times \left[\vec{\Omega} \times \hat{u} - \vec{\Gamma} \cdot \hat{u}\right]
\end{aligned}
$$

Since $\hat{u} \times \left(\vec{\Omega} \times \hat{u}\right) = \vec{\Omega}$, we have

$$
\vec{\tau}^h = -\gamma_r \left[\vec{\Omega} - \hat{u} \times \left(\vec{\Gamma} \cdot \hat{u}\right)\right]
$$

where

$$
\gamma_r = C_\perp D^2 \sum_j j^2 = C_\perp D^2 \frac{1}{12}\left(\frac{L}{D}\right)^3
$$

In the case of $\vec{\Gamma} = 0$, $C_\perp$ must be equal to the constant C in eqn.(5.130), that is, γ_r is nothing but the rotational friction coefficient in eqn.(5.134).

Alternatively the sums in the previous equation can be calculated, as in the book (see eqns. (5.121, 5.122)

$$
1 + \frac{3}{8}\frac{1}{n+1}\sum_{j=-\frac{n}{2}}^{\frac{n}{2}} \sum_{i=-\frac{n}{2}, i \neq j}^{\frac{n}{2}} \left\{\frac{2}{|i-j|} - \frac{1}{6}\frac{1}{|i-j|^3}\right\} \simeq \frac{3}{2}\ln\left(\frac{L}{D}\right)
$$

$$
\frac{3}{8}\frac{1}{n+1}\sum_{j=-\frac{n}{2}}^{\frac{n}{2}} \sum_{i=-\frac{n}{2}, i \neq j}^{\frac{n}{2}} \left\{\frac{1}{|i-j|} + \frac{1}{12}\frac{1}{|i-j|^3}\right\} \simeq \frac{3}{4}\ln\left(\frac{L}{D}\right)
$$

(b) Consider a rod in uniform translational motion with a velocity $\vec{v}$, without any rotation.

The force on bead i is again proportional to the relative velocity of that bead to the local imposed shear flow velocity. Similar to (a), the force is decomposed in a component parallel and perpendicular to the rod's long axis leading to a total force equal to

$$\vec{F}_i^h = -C_{\|}\hat{u}\hat{u}\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_i\right) - C_{\perp}\left[\hat{I}-\hat{u}\hat{u}\right]\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_i\right)$$

$$= -C_{\|}\hat{u}\hat{u}\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_c - iD\vec{\Gamma}\cdot\hat{u}\right) - C_{\perp}\left[\hat{I}-\hat{u}\hat{u}\right]\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_c - iD\vec{\Gamma}\cdot\hat{u}\right)$$

In the second line we used that $\vec{r}_i = \vec{r}_c + iD\,\hat{u}$, where $\vec{r}_c$ is the position of the center of the rod. The total force on the rod is thus equal to

$$\vec{F}^h = \sum_i \vec{F}_i^h = -\gamma_{\|}\,\hat{u}\,\hat{u}\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_c\right) - \gamma_{\perp}\left(\hat{I}-\hat{u}\,\hat{u}\right)\cdot\left(\vec{v}-\vec{\Gamma}\cdot\vec{r}_c\right)$$

where

$$\gamma_{\|} = C_{\|}\frac{L}{D}, \quad \gamma_{\perp} = C_{\perp}\frac{L}{D}$$

Without shear flow, it follows that $\gamma_{\|}$ and $\gamma_{\perp}$ are nothing but the translational friction coefficients given in eqn. (5.125, 5.126).

The translational velocity of a rod in terms of the hydrodynamic is found by inversion of the formula for the force in terms of the velocity

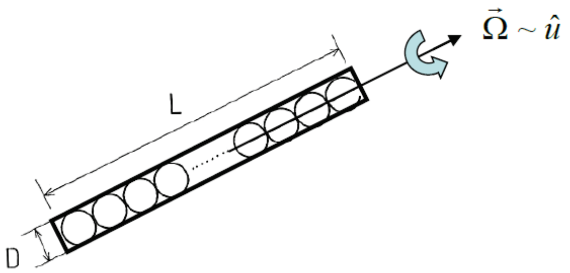
$$\boxed{\vec{v} = \vec{\Gamma}\cdot\vec{r}_c - \frac{1}{\gamma_{\|}}\hat{u}\,\hat{u}\cdot\vec{F}^h - \frac{1}{\gamma_{\perp}}\left(\hat{I}-\hat{u}\,\hat{u}\right)\cdot\vec{F}^h}$$

where the friction coefficients are those for motion in an otherwise quiescent solvent

$$\gamma_{\|} = \frac{2\pi\eta_0 L}{\ln\left(L/D\right)} \quad \text{and} \quad \gamma_{\perp} = \frac{4\pi\eta_0 L}{\ln\left(L/D\right)}$$

5.10 Friction of a long and thin rod, rotating around its long axis

Here we consider a rod rotating along its long axis (see the figure below), in an otherwise quiescent solvent. As before, the rotational velocity is denoted by $\vec{\Omega}$ while its center is at the origin. For a rod rotating along its long axis, the angular velocity is parallel to the orientation $\hat{u}$ of the rod. The positions of all beads remain unchanged, and each bead rotates with the same angular velocity.



To obtain the friction coefficient of this rotational motion, Faxen's theorem for rotational motion of a single sphere can be used

$$\vec{\Omega}_j = -\frac{1}{\pi \eta_0 D^3} \vec{\tau}_j^h + \frac{1}{2} \nabla_j \times \vec{u}_0 \left(\vec{r}_j \right)$$

where $\vec{\tau}_j^h$ is the hydrodynamic torque on bead *j*, and $\vec{u}_0(\vec{r}_j)$ is the flow velocity due to the remaining beads, in the absence of bead *j*. The fluid flow field that originates form a single rotating sphere is

$$\vec{u}\left(\vec{r}\right) = \left(\frac{a}{r}\right)^3 \vec{\Omega} \times \vec{r}$$

which is zero at the positions $\vec{r} \sim \vec{\Omega} \sim \hat{u}$. The conclusion from this is that hydrodynamic interactions between beads are in this case not important. Only reflection terms come into play here, which are of lower order in the inverse aspect ratio.

The fluid flow field $\vec{u}_0(\vec{r}_j)$ that bead *j* experiences due to the rotation the other beads is small, and tends to zero for large distances between the two beads. This implies that for long and thin rods, hydrodynamic interactions between the beads may be neglected, so that only the Stokes friction term (the first term) is of important.

Since hydrodynamic forces on the beads are thus equal to that of single rotating sphere, the torque on the rod is equal to the sum of individual bead-torques, and hence, according to Faxen's theorem

$$\vec{\tau}^{\,h} = \sum_{j=-n/2}^{n/2} \vec{\tau}_j = -\pi\,\eta_0 D^3 \sum_{j=-n/2}^{n/2} \vec{\Omega}_j = -\pi\,\eta_0 D^3 N \vec{\Omega}$$

where $N=L/D$ is the total number of beads. Hence

$$\boxed{\vec{\tau}^{\,h} = -\gamma_{r,\parallel}\,\vec{\Omega}}$$

with $\gamma_{r,\parallel}$ the friction coefficient for parallel rotation

$$\boxed{\gamma_{r,\parallel} = \pi\,\eta_0 L D^2}$$

This friction coefficient is to be compared to the one for perpendicular rotation, as considered in the book

$$\gamma_{r,\perp} = \frac{\pi\,\eta_0 L^3}{3\ln(L/D)}$$

The ratio of the two is very small

$$\frac{\gamma_{r,\perp}}{\gamma_{r,\parallel}} = \frac{1}{3\ln(L/D)}\left(\frac{L}{D}\right)^2 \gg 1$$

Exercises Chapter 6: DIFFUSION

Courtesy of Guy Fontdeville, Int. Graphics GmbH, Germany

6.1 Non-Gaussian behavior of displacements

For a Gaussian Brownian displacements, the self-dynamic structure factor $S_S(k,t)$ was shown to be related to the mean squared displacement $< R^2 >$ as

$$S_S(k,t) = \exp\left(-\frac{1}{6}k^2\left\langle R^2\right\rangle\right)$$

To discuss the non-Gaussian contributions, we start with the definition of the structure factor (with $\Delta\vec{r} = \vec{r}(t) - \vec{r}(0)$)

$$\begin{aligned} S_S(k,t) &\equiv \left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}(t=0)-\vec{r}(t)\right)\right]\right\rangle \\ &= \int d\Delta\vec{r}\, P\left(\Delta\vec{r},t\right) e^{-i\vec{k}\cdot\Delta\vec{r}} \end{aligned}$$

For an isotropic system, the pdf $P(\Delta\vec{r},t)$ depends only on the magnitude of the displacement $|\Delta\vec{r}|$, not on its direction. Integration with respect to the direction of $\Delta\vec{r}$ can be done as follows (with $R = |\Delta\vec{r}|$)

$$\begin{aligned} S_S(k,t) &= \int d\Delta\vec{r}\, P\left(\Delta\vec{r},t\right) e^{-i\vec{k}\cdot\Delta\vec{r}} \\ &= \frac{1}{4\pi}\int_0^\infty dR\, R^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, P(R,t)\, e^{-ikR\cos\theta} \end{aligned}$$

$$
\begin{aligned}
S_S(k,t) &= \frac{1}{2}\int_0^\infty dR\, R^2 P(R,t)\int_{-1}^{1} dx\, e^{-ikRx} \\
&= \int_0^\infty dR\, R^2 P(R,t)\frac{\sin(kR)}{kR} \\
&= \frac{1}{k}\int_0^\infty dR\, R\sin(kR)P(R,t)
\end{aligned}
$$

Then use the series expansion of sin(x) as

$$\sin x = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 + \cdots$$

to obtain

$$
\begin{aligned}
S_S(k,t) &= \frac{1}{k}\int_0^\infty dR\, R\left(kR - \frac{(kR)^3}{6} + \frac{(kR)^5}{120} + \cdots\right)P(R,t) \\
&= 1 - \frac{k^2}{6} < R^2 > + \frac{k^4}{120} < R^4 > + \text{"O}(k^6)\text{"}
\end{aligned}
$$

where

$$\left\langle \left|\Delta\vec{r}\right|^n \right\rangle \equiv \int_0^\infty dR\, R^{2+n} P(R,t)$$

and where it is used that normalization implies

$$1 = \int_0^\infty dR\, R^2 P(R,t)$$

Re-exponentiation of the above formula, using that $e^x = 1 + x + \frac{1}{2}x^2 + \cdots$, it is found that, again up to order k^4

$$\boxed{S_S(k,t) = \exp\left(-\frac{1}{6}k^2\left\langle R^2\right\rangle + \frac{1}{360}k^4\left[3\left\langle R^4\right\rangle - 5\left\langle R^2\right\rangle^2\right]\right)}$$

We will now show that for a Gaussian pdf, the terms $\sim k^4$ vanish. The Gaussian form reads

$$P(\vec{R},t) = N e^{-\alpha R^2} \quad , \quad N = \left(\frac{\alpha}{\pi}\right)^{3/2}$$

where α is related to the mean squared displacement. Hence

$$< R^2 >= N\int d\vec{R}\, R^2 e^{-\alpha R^2} = 4\pi N \int_0^\infty dR\, R^4 e^{-\alpha R^2}$$

$$= 4\pi N \left(\frac{\partial^2}{\partial \alpha^2} \int_0^\infty dR\, e^{-\alpha R^2} \right) = 4\pi N \left(\frac{1}{2} \frac{\partial^2}{\partial \alpha^2} \sqrt{\frac{\pi}{\alpha}} \right) = \frac{3\pi}{2} N \sqrt{\pi}\, \alpha^{-5/2}$$

and

$$< R^4 >= 4\pi N \int_0^\infty dR\, R^6 e^{-\alpha R^2} = -4\pi N \left(\frac{\partial^3}{\partial \alpha^3} \int_0^\infty dR\, e^{-\alpha R^2} \right)$$

$$= -4\pi N \left(\frac{1}{2} \frac{\partial^3}{\partial \alpha^3} \sqrt{\frac{\pi}{\alpha}} \right) = \frac{15\pi}{4} N \sqrt{\pi}\, \alpha^{-7/2}$$

and therefore

$$3\left\langle R^4 \right\rangle - 5\left\langle R^2 \right\rangle^2 = 3\left(\frac{15\pi}{4} N \sqrt{\pi}\, \alpha^{-7/2} \right) - 5\left(\frac{3\pi}{2} N \sqrt{\pi}\, \alpha^{-5/2} \right)^2$$

$$= \frac{45\pi}{4} \left(\frac{\alpha}{\pi} \right)^{3/2} \sqrt{\pi}\, \alpha^{-7/2} - \frac{45\pi^2}{4} \left(\frac{\alpha}{\pi} \right)^3 \pi\, \alpha^{-5} = 0$$

This indeed shows that the higher order wave vector dependence vanishes for a Gaussian pdf.

The experimental determination of the non-Gaussian terms goes as follows:

Plotting $\dfrac{6 \ln S_S(k,t)}{k^2}$ as a function of k^2, which gives a straight line.
According to the above expression for the structure factor we have

$$\frac{6 \ln S_S(k,t)}{k^2} = -< R^2 > + \frac{1}{60} k^4 \left[3\left\langle R^4 \right\rangle - 5\left\langle R^2 \right\rangle^2 \right]$$

The intercept of the straight line gives $-< R^2 >$, while and the slope characterizes the non-Gaussian contributions to the pdf.

6.4 Gradient diffusion

Without hydrodynamic interaction, the first order in volume fraction coefficient is

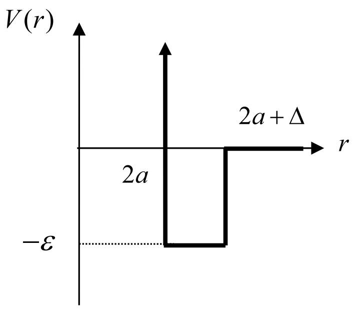
$$\alpha_{\nabla} = -\beta \int_0^\infty dx\, x^3 g^{(0)}(ax) \frac{dV(ax)}{dx}$$

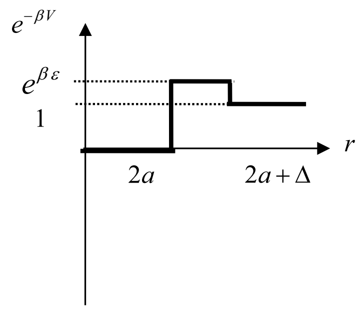
where $g^{(0)} = \exp(-\beta V)$ is the pair-correlation function to leading order in concentration.

In this exercise we consider the case where, in addition to hard-core interactions, there is an attractive square-well interaction potential

$$V^+(r) = \begin{cases} 0, & 0 \le r \le 2a \\ -\varepsilon, & 2a < r < 2a + \Delta \\ 0, & r \ge 2a + \Delta \end{cases}$$

where ε is the depth of the square-well, and Δ is its width.





This potential is sketched in the left figure above. Note that $\varepsilon > 0$.

We need to evaluate the combination $g^{(0)}(r)\, dV(r)/dr$ in order to evaluate the integral. Since

$$g^{(0)}(r)\frac{dV(r)}{dr} = e^{-\beta V}\,\frac{dV(r)}{dr} = -\frac{1}{\beta}\frac{d\left(e^{-\beta V(r)}\right)}{dr}$$

we have

$$\alpha_{\nabla} = \int_0^\infty dx\, x^3\, \frac{d\exp\left\{-\beta\left[V_{hc}(ax) + V^+(ax)\right]\right\}}{dx}$$

where V_{hc} is the hard-core part of the potential. Noting the right figure above (where we have $V = V_{hc} + V^+$),

$$\alpha_\nabla = \int_0^\infty dx\, x^3 \left[e^{\beta\varepsilon}\delta(x-2) - \left(e^{\beta\varepsilon}-1\right)\delta\left(x-2-\frac{\Delta}{2}\right)\right]$$
$$= \left[8\, e^{\beta\varepsilon} - \left(2+\frac{\Delta}{2}\right)^3 \left(e^{\beta\varepsilon}-1\right)\right] = 8 - \left(e^{\beta\varepsilon}-1\right)\left[\left(2+\frac{\Delta}{2}\right)^3 - 8\right]$$

where δ is the delta distribution. This result is obtained from the fact that the derivative of a function that makes a jump, is equal to the delta distribution at the coordinate where the jump occurs, multiplied by the height of the jump. The first contribution (equal to *8*) is the hard-core contribution, while the second term is due to the attractive square-well potential.

The equation of motion for the density thus reads

$$\frac{\partial}{\partial t}\rho\left(\vec{r},t\right) = D\,\nabla^2\rho\left(\vec{r},t\right) \qquad \text{with} \qquad D = D_0\left(1+\alpha_\nabla\,\varphi\right)$$

Question: Is diffusion enhanced or slowed down due to attractive interactions?
For $\varepsilon > 0$, that is $e^{\beta\varepsilon} - 1 > 0$, the attractive potential is seen to lower the diffusion coefficient. Attractions generally diminish the diffusion coefficient.

The combination $1+\alpha_\nabla\,\varphi$ can be made negative for strong attractions, which implies that the gradient diffusion coefficient is negative, so that gradients in the density increase their amplitude in time. Particles now diffuse from regions of low concentration, to regions of high concentration, which is commonly referred to as “uphill diffusion”. This is the case when the system is thermodynamically unstable. In that case, the system does not relax to the homogeneous state, but rather develops inhomogeneities. This is the initial stage of phase separation.

Up to first order in concentration, a negative diffusion coefficient is nothing more than a formal result. When the first order in volume fraction contribution is now large in magnitude than the zero order term, the higher order terms in concentration cannot be neglected. This exercise can be a good practice for the calculation of the spinodal phase separation, which will be the part of the kinetics of the phase separation in Chapter 9.

6.5 An effective medium approach

To within an effective medium approach, it is tempting to identify an effective friction coefficient γ^{eff}, for dilute suspensions, which is defined as

$$\gamma^{eff} = 6\pi\eta^{eff} a = 6\pi\eta_0 a\left(1+\frac{5}{2}\varphi\right) \quad \text{where} \quad \eta^{eff} = \eta_0\left(1+\frac{5}{2}\varphi\right)$$

This friction coefficient is interpreted as the friction coefficient of a sphere that includes interactions with other spheres.

The true friction coefficient, to leading order in concentration, has been derived (see eqn.(6.129)), with the result

$$\gamma^{eff} = \frac{k_B T}{D_0}\frac{1}{1-2.11\varphi+O\left(\varphi^2\right)} = \gamma_0\left[1+2.11\,\varphi+O\left(\varphi^2\right)\right]$$

This is on odds with the first equation. Although the difference (*2.50* instead of *2.11*) is not large, there is a fundamental reason why the effective medium approach is wrong.

The contribution $(5/2)\varphi$ in the effective medium approach is independent of the type of interactions, and is fully determined by the stress that is generated by a single sphere in shear flow. The contribution 2.11φ in the exact expression for the effective friction coefficient does depend on the type in interactions (this particular value is for hard-sphere interactions).

Effective medium approaches can be accurate for large concentrations, where inter-particle interactions are important for both the effective viscosity and the effective friction coefficient. A very early version of an effective medium theory is due to Brinkman.

6.6 Long-time self-diffusion without hydrodynamic interaction

In this exercise we repeat the analysis of section 6.7 with the neglect of hydrodynamic interactions. This simplifies the calculation considerably.

The thermally averaged velocity of the probe particle number 1 is

$$\left\langle \vec{v}_1 \right\rangle = -\beta \left\langle \sum_{j=1}^{N} \vec{D}_{1j} \cdot \vec{F}_j^h \right\rangle$$

Without hydrodynamic interactions we have

$$\vec{D}_{1j} = \delta_{1j} D_0 \, \hat{I} \qquad (1)$$

so that

$$\left\langle \vec{v}_1 \right\rangle = -\beta D_0 \left\langle \vec{F}_1^h \right\rangle$$

Since there is a force balance

$$\vec{F}_1^h - \nabla_1 \Phi - k_B T \, \nabla_1 \ln P + \vec{F}^{ext} = \vec{0}$$

the average velocity can also be written as

$$\left\langle \vec{v}_1 \right\rangle = \beta D_0 \left\{ \vec{F}^{ext} - \left\langle \nabla_1 \Phi \right\rangle - k_B T \left\langle \nabla_1 \ln P \right\rangle \right\} \qquad (2)$$

Note that, according to eq.1 with $i{=}j$, the first term $\beta D_0 \, \vec{F}^{ext}$ is noting but $\beta \left\langle \vec{D}_{11} \right\rangle \cdot \vec{F}^{ext}$, which corresponds to the statement in (a) in the book. In the present case, the above equation is written as

$$\left\langle \vec{v}_1 \right\rangle = \beta D_0 \, \vec{F}^{ext} + \left\langle \vec{v}_1^{\,I} \right\rangle + \left\langle \vec{v}_1^{\,Br} \right\rangle \qquad (2b)$$

where

$$\begin{aligned} \left\langle \vec{v}_1^{\,I} \right\rangle &= -\beta D_0 \left\langle \nabla_1 \Phi \right\rangle \\ \left\langle \vec{v}_1^{\,Br} \right\rangle &= -D_0 \left\langle \nabla_1 \ln P \right\rangle \end{aligned} \qquad (2c)$$

In order to calculate the averages, we have to solve the Smoluchowski equation, which reads, neglecting hydrodynamic interactions

$$0 = \nabla \cdot \left[2\nabla P + 2\beta P \, \nabla V\left(r\right) - \beta P \, \vec{F}^{ext} \right] \qquad (3)$$

Here, P is the pdf with respect to which the averages must be calculated. We make the same expansion as in the book of the pdf to leading order in the external force

$$P(\vec{r}) = P^{(0)}\left(r\right)\left[1+\beta a\, L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\right]$$
$$= \frac{1}{V^2} e^{-\beta V(r)}\left[1+\beta a\, L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\right]$$

where $P^{(0)}\left(r\right) = e^{-\beta V(r)}/V^2$ is the pdf without the external field (with V the volume of the system). Substitution into the Smoluchowski eqn. (3) gives

$$0 = \nabla\cdot\left[2\beta a\nabla\left(e^{-\beta V(r)}L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\right)+2\beta^2 a\; e^{-\beta V(r)}L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\left(\nabla V\left(r\right)\right)-\beta e^{-\beta V(r)}\vec{F}^{ext}\right]$$

up to linear order in the external force. This is equivalent to

$$0 = \nabla\cdot e^{-\beta V(r)}\left[2a\nabla\left(L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\right)-\vec{F}^{ext}\right] \qquad (4)$$

For hard-core interactions, where

$$e^{-\beta V(r)} \equiv 1 \quad \text{for} \quad r \geq 2a$$

we thus have

$$\nabla^2\left(L\left(r\right)\hat{r}\cdot\vec{F}^{ext}\right) = 0\,; \quad r \geq 2a$$

Now let $\vec{F}^{ext} = F^{ext}\,\hat{e}_z$ with $\hat{e}_z = (0,0,1)$, so that

$$\hat{r}\cdot\vec{F}^{ext} = \left(\hat{r}\cdot\hat{e}_z\right)F^{ext} = \frac{z}{r}F^{ext} = \cos\theta\, F^{ext}$$

and hence

$$\nabla^2\left(L\left(r\right)\cos\theta\, F^{ext}\right) = 0\,; \quad r \geq 2a$$

In spherical coordinates this reads

$$\frac{1}{r}\cos\theta\frac{d^2}{dr^2}\left(rL(r)\right)+L(r)\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\cos\theta}{d\theta}\right) = 0$$

and hence

$$r^2\frac{d^2L\left(r\right)}{dr^2}+2r\frac{dL\left(r\right)}{dr}-2L = 0$$

With the trial function $L\left(r\right) = C/r^n$, where C is the constant, one finds after substitution that $n^2-n-2=0$ so that the Ansatz is a solution for $n=2$

$$L\left(r\right) = \frac{C}{r^2} \qquad \text{for} \quad r \geq 2a \qquad (5)$$

The constant C has yet to be determined. This can be done through integration of eqn. (4) from $r_- = 2a - \varepsilon$ to $r_+ = 2a + \varepsilon$, where ε is an arbitrary small length. To do this, note that there are terms in the Smoluchowski eqn.(4) that exhibit a delta-singularity at $r=2a$. These contributions give a finite contribution on integration, while continuous contributions, or terms that show a finite jump discontinuity, give a zero result for vanishing ε . Note that, for hard-core interactions

(i) $$\vec{F}^{ext} \cdot \nabla e^{-\beta V(r)} = F^{ext} \frac{\partial}{\partial z} e^{-\beta V(r)} = F^{ext} \frac{\partial r}{\partial z} \frac{d}{dr} e^{-\beta V(r)} = F^{ext} \cos\theta \, \delta\left(r - 2a\right)$$

(ii) $$-2a \nabla \left(L\left(r\right) \hat{r} \cdot \vec{F}^{ext}\right) \cdot \nabla e^{-\beta V(r)} = -2a \left[\frac{d}{dr}\left(L\left(r\right) \cos\theta F^{ext}\right)\right] \frac{d}{dr} e^{-\beta V(r)}$$
$$= 2aF^{ext} \cos\theta \, \frac{dL(r)}{dr} \delta\left(r - 2a\right)$$

(iii) $$2a \, e^{-\beta V(r)} \nabla^2 \left(L\left(r\right) \hat{r} \cdot \vec{F}^{ext}\right) = 0$$

Using these identities, integration of eqn.(4) from $r_- = 2a - \varepsilon$ to $r_+ = 2a + \varepsilon$ for vanishing ε , leads to

$$1 - 2a \left.\frac{dL(r)}{dr}\right|_{r=2a} = 0$$

From eqn. (5) it thus follows that $C = -2a^2$, and hence

$$L\left(r\right) = -2\left(\frac{a^2}{r^2}\right)$$

which is the result (b) in the exercise.

Since we now have determined the pdf, we can calculate the averages in eqns. (2c). Since the interaction potential is the sum of pair-wise potential of two different particles as

$$\Phi = \sum_{n<m} V(r_{nm}) \quad , \quad r_{nm} = \left|\vec{r}_n - \vec{r}_m\right|$$

and hence

$$\nabla_1 \Phi = \sum_{m=2}^{N} \nabla_1 V(r_{1m})$$

it follows that

$$\begin{aligned}\left\langle \vec{v}_1^{\,I} \right\rangle &= -\beta D_0 \sum_{m=2}^{N} \left\langle \nabla_1 V(r_{1m}) \right\rangle = -\beta D_0 \left(N-1\right) \left\langle \nabla_1 V(r_{12}) \right\rangle \\ &= -\beta D_0 \left(N-1\right) \int d\vec{r}_1 \cdots \int d\vec{r}_N P\left(\vec{r}_1, \cdots \vec{r}_N\right) \nabla_1 V(r_{12}) \\ &= -\beta D_0 \left(N-1\right) \int d\vec{r}_1 \int d\vec{r}_2 P\left(\vec{r}_1, \vec{r}_2\right) \nabla_1 V(r_{12}) \\ &= -\beta D_0 \left(N-1\right) V \int d\vec{r} P\left(\vec{r}\right) \nabla V(r)\end{aligned}$$

with $\vec{r} = \vec{r}_1 - \vec{r}_2$.

Substitution of the pdf that we found gives, for sufficiently large numbers of particles ($N \gg 1$)

$$\left\langle \vec{v}_1^{\,I} \right\rangle = -\beta D_0 \frac{N}{V} \int d\vec{r}\, e^{-\beta V(r)}\, \nabla V(r) - \beta^2 a D_0 \frac{N}{V} \vec{F}^{ext} \cdot \int d\vec{r}\, \hat{r} L(r) e^{-\beta V(r)}\, \nabla V(r)$$

Since $e^{-\beta V(r)}\, \nabla V(r) = \nabla e^{-\beta V(r)} = \hat{r}\, \delta\left(r - 2a\right)$, angular integrals render the first contribution as zero. The second terms gives (with $\hat{e}_z = (0,0,1)$; note that $\vec{F}^{ext}$ is along the *z*-direction)

$$\begin{aligned}\left\langle \vec{v}_1^{\,I} \right\rangle &= -\beta^2 a D_0 \frac{N}{V} F^{ext} \left(-\frac{1}{\beta} \int d\vec{r}\, \frac{z}{r} L(r) \nabla e^{-\beta V(r)} \right) \\ &= \beta a D_0 \frac{N}{V} F^{ext} \left(\int d\vec{r}\, L(r) \frac{z}{r} \frac{\vec{r}}{r} \delta\left(r - 2a\right) \right) \\ &= \beta a D_0 \frac{N}{V} \vec{F}^{ext} \left(\int d\vec{r}\, L(r) \cos^2\theta\, \delta\left(r - 2a\right) \right) \\ &= \beta D_0 \frac{N}{V} a \vec{F}^{ext}\, 2\pi \int_0^{\pi} d\theta \sin\theta \cos^2\theta \int_0^{\infty} dr\, r^2 L(r)\, \delta\left(r - 2a\right)\end{aligned}$$

Both integrals can be easily calculated, leading to the statement (c) in the book

$$\left\langle \vec{v}_i^{\,I} \right\rangle = -\beta D_0\, 2\varphi \vec{F}^{ext}$$

where the volume fraction is defined as $\varphi = \frac{N}{V} \frac{4\pi}{3} a^3$.

Last the Brownian velocity in eqn. (2c) is equal to

$$\begin{aligned}\left\langle \vec{v}_1^{\,Br} \right\rangle &= -D_0 \left\langle \nabla_1 \ln P \right\rangle \\ &= -D_0 \int d\vec{r}_1 \cdots \int d\vec{r}_N P\left(\vec{r}_1, \cdots \vec{r}_N\right) \nabla_1 \ln P\left(\vec{r}_1, \cdots \vec{r}_N\right) \\ &= -D_0 \int d\vec{r}_1 \cdots \int d\vec{r}_N \nabla_1 \ln P\left(\vec{r}_1, \cdots \vec{r}_N\right) \\ &= -D_0 \int d\vec{r}_1 \nabla_1 P\left(\vec{r}_1\right)\end{aligned}$$

Since $P(\vec{r}_1)$ is constant (being proportional to the macroscopic density), and thus leads to the result (d) in the exercise

$$\left\langle \vec{v}_1^{Br} \right\rangle = \vec{0}$$

It is thus found form eqn. (2b) that the total averaged translational velocity is

$$\left\langle \vec{v}_1 \right\rangle = \beta D_0 \, \vec{F}^{ext} + \left\langle \vec{v}_1{}^{I} \right\rangle + \left\langle \vec{v}_1{}^{Br} \right\rangle = \beta D_0 \, \vec{F}^{ext} \left\{1 - 2\varphi\right\}$$

By definition, the effective frictional coefficient is thus equal to

$$\gamma^{eff} \left\langle \vec{v}_1 \right\rangle = \vec{F}^{ext} \quad \Rightarrow \quad \gamma^{eff} = \frac{1}{\beta \, D_0 \left\{1 - 2\varphi\right\}}$$

and therefore, from Einstein's relation $D_S^L = \dfrac{k_B T}{\gamma^{eff}}$ the long-time self-diffusion coefficient is found to be equal to

$$\boxed{D_S^L = D_0 \left\{1 - 2\varphi\right\}}$$

This expression neglects quadratic and higher order terms in the volume fraction.

6.11 Depolarization of light by scattering

The scattering amplitude $\vec{\vec{B}}$ of an optically homogeneous, thin and long rod (like fd-viruses) is proportional to

$$\vec{\vec{B}} \sim \bar{\varepsilon}\hat{I} + \Delta\varepsilon\left(\hat{u}\hat{u} - \frac{1}{3}\hat{I}\right)$$

Suppose that the orientation $\hat{u}$ of the rod lies the x-z plane, which is spanned by the polarization directions $\hat{n}_0$ and $\hat{n}_s$ of the incident and scattered radiation, respectively (see the figure below). The polarization of the incident light is along the *z*-direction, and of the scattered light along the *x*-direction (see also Fig.6.18 in the book)

$$\hat{n}_0 = (0,0,1)$$
$$\hat{n}_S = (1,0,0)$$

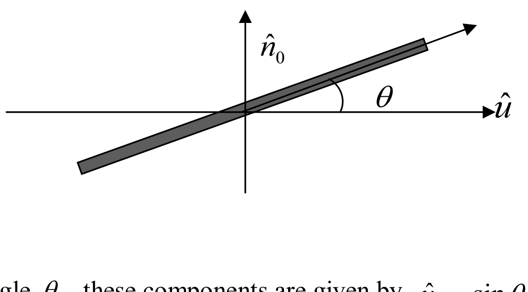
Let θ be the angle between $\hat{u}$ and the x-axis (as depicted in the figure below).

The dipole that is induced in the core of the rod is proportional to $\vec{\vec{B}}\cdot\hat{n}_0$, which is in turn proportional the scattered electric field at large distance from the rod. The component of the detected scattered electric field is along $\hat{n}_s$, that is, the detected scattered electric field strength is proportional to $\hat{n}_0\cdot\vec{\vec{B}}\cdot\hat{n}_s$.

The scattered intensity is thus proportional to $(\hat{n}_0\cdot\vec{\vec{B}}\cdot\hat{n}_s)^2$. Note that there is a mistake in the exercise in the book, in that the square of the electric field is not taken to arrive at the intensity. From the above expression for the scattering amplitude we get

$$\hat{n}_0\cdot\vec{\vec{B}}\cdot\hat{n}_s = \Delta\varepsilon\,\hat{u}_z\,\hat{u}_x$$

where $\hat{u}_x$ and $\hat{u}_z$ are the x- and z-components of $\hat{u}$, respectively.



In terms of the angle θ , these components are given by $\hat{u}_z = \sin\theta, \hat{u}_x = \cos\theta$

so that

$$\hat{n}_0\cdot\vec{\vec{B}}\cdot\hat{n}_s \sim \Delta\varepsilon\sin\theta\cos\theta$$

The scattered intensity amplitude I is therefore $I \sim (\sin\theta\cos\theta)^2$

The maximum scattered intensity occurs for those angles such that the following conditions are satisfied

$$\left.\begin{aligned}\frac{\partial}{\partial\theta}\left(\hat{n}_0\cdot\vec{B}\cdot\hat{n}_s\right)^2 &= 0\\ \frac{\partial^2}{\partial\theta^2}\left(\hat{n}_0\cdot\vec{B}\cdot\hat{n}_s\right)^2 &< 0\end{aligned}\right\}$$

Performing the differentiations, this gives

$$\begin{aligned}\sin\theta\cos\theta\left[\cos^2\theta-\sin^2\theta\right] &= \frac{1}{2}\sin(2\theta)\cos(2\theta)\\ &= \frac{1}{4}\sin(4\theta)=0\end{aligned}$$

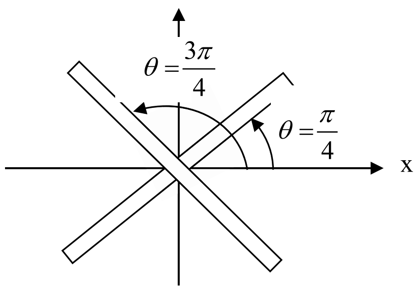
and

$$\cos(4\theta)<0$$

The first condition gives the solutions $4\theta = 0,\pi,2\pi,3\pi,\cdots$. Since $0\le\theta<\pi$, the only relevant solutions are $\theta = 0,\pi/4,\pi/3,3\pi/4$. The second condition selects the solutions which correspond to a maximum in the scattered intensity (the remaining solutions of the first condition correspond to a minimum). The maximum scattered intensity thus occurs when

$$\theta=\frac{\pi}{4} \qquad \text{and} \qquad \theta=\frac{3\pi}{4}$$

These orientations are depicted in the figure below.



6.12 Orientational relaxation of rods

Here we consider an assembly of interacting rods which are oriented along the *z*-axis at time $t = 0$, and calculate the average orientation

$$\left\langle \hat{u}_1(t) \right\rangle = \oint d\hat{u}_1\, \hat{u}_1 P\left(\hat{u}_1, t\right)$$

after release of the constraint that keeps the rods aligned along the *z*-axis. Using eq.(6.243) immediately leads to

$$\begin{aligned} \left\langle \hat{u}_{z1} \right\rangle &= \oint d\hat{u}\, \hat{u}_{z1} P\left(\hat{u}_1, t\right) \\ &= \sqrt{\frac{4\pi}{3}} \sum_{l=0}^{m} \sum_{m=-l}^{l} Y_l^{m,*}\left(\hat{e}_3\right) \oint d\hat{u}\, Y_1^{0,*}\left(\hat{u}_1\right) Y_l^m\left(\hat{u}_1\right) \\ &\times \left[\mathrm{e}^{-D_r l(l+1)t} + \bar{\rho} D_r \int_0^t dt'\, \gamma_{1m}(t')\, \mathrm{e}^{-D_r l(l+1)(t-t')} \right] \end{aligned}$$

where it is used that $u_{1,z} = \sqrt{4\pi/3}\, Y_l^{0,*}\left(\hat{u}\right)$, and $\hat{e}_3 = (0,0,1)$ is the initial orientation. Note that there is a mistake in eqn (6. 243): the pre-facto $\sqrt{(2l+1)/4\pi}$ is not correct, and should be omitted. Now use orthogonality of spherical harmonics

$$\oint d\hat{u}\, Y_l^{m*}\left(\hat{u}\right) Y_{l'}^{m'}\left(\hat{u}\right) = \delta_{ll'} \delta_{mm'}$$

so that

$$\begin{aligned} \left\langle \hat{u}_{z1} \right\rangle &= \sqrt{\frac{4\pi}{3}}\, Y_1^{0,*}\left(\hat{e}_3\right) \left[\mathrm{e}^{-2D_r t} + \bar{\rho} D_r \int_0^t dt'\, \gamma_{10}(t')\, \mathrm{e}^{-2D_r (t-t')} \right] \\ &= \mathrm{e}^{-2D_r t} + \bar{\rho} D_r \int_0^t dt'\, \gamma_{10}(t')\, \mathrm{e}^{-2D_r (t-t')} \end{aligned}$$

According to eqn. (6.242), the coefficient γ_{10} is equal to

$$\gamma_{10}(t) = \beta \oint d\hat{u}_1 Y_1^{0*}\left(\hat{u}_1\right) \hat{\Re}_1 \cdot \left[P^{(0)}\left(\hat{u}_1, t\right) \oint d\hat{u}_2\, \vec{T}_1\left(\hat{u}_1, \hat{u}_2\right) P^{(0)}\left(\hat{u}_2, t\right) \right]$$

From eqn. (6.240) and eqn (6.245), we get eqn. (6.246) as the mean-field approximation of this coefficient

$$\begin{aligned} \oint d\hat{u}_2\, \vec{T}_1\left(\hat{u}_1, \hat{u}_2\right) P^{(0)}\left(\hat{u}_2, t\right) &\approx \vec{T}\left(\hat{u}_1, \left\langle \hat{u}_2(t) \right\rangle_0\right) \\ &= 2\beta^{-1} D L^2\, \hat{u}_{z1} \frac{\hat{u}_1 \times \hat{e}_3}{\left|\hat{u}_1 \times \hat{e}_3\right|} e^{-2D_r t} \end{aligned}$$

Substitution thus leads to

$$\gamma_{10}\left(t\right) \approx 2DL^2\, e^{-2D_r t} \oint d\hat{u}_1 Y_1^{0*}\left(\hat{u}_1\right) \hat{\Re}_1 \cdot \left[P^{(0)}\left(\hat{u}_1, t\right) \hat{u}_{z1} \frac{\hat{u}_1 \times \hat{e}_3}{\left|\hat{u}_1 \times \hat{e}_3\right|} \right]$$

$$= -2DL^2\, e^{-2D_r t} \oint d\hat{u}_1 \left[P^{(0)}\left(\hat{u}_1, t\right) \hat{u}_{z1} \frac{\hat{u}_1 \times \hat{e}_3}{\left|\hat{u}_1 \times \hat{e}_3\right|} \right] \cdot \hat{\Re}_1 Y_1^{0*}\left(\hat{u}_1\right)$$

where a partial integration has been done. This is eqn.(6.247) where both p is *1* and q is *0*. Since

$$Y_1^0\left(\hat{u}_0\right) = \sqrt{\frac{3}{4\pi}}\, \hat{u}_{z1}$$

so that

$$\hat{\Re}_1 Y_1^{0*}\left(\hat{u}_1\right) = \sqrt{\frac{3}{4\pi}}\, \hat{u}_{z1} \times \hat{e}_3$$

Using again a similar mean-field approximation

$$\gamma_{10}\left(t\right) = -2DL^2\, e^{-2D_r t} \sqrt{\frac{3}{4\pi}} \oint d\hat{u}_1\, P^{(0)}\left(\hat{u}_1, t\right) \hat{u}_{z1} \left|\hat{u}_1 \times \hat{e}_3\right|$$

$$= -2DL^2\, e^{-2D_r t} \sqrt{\frac{3}{4\pi}} \oint d\hat{u}_1\, P^{(0)}\left(\hat{u}_1, t\right) \hat{u}_{z1} \sqrt{1 - \hat{u}_{z1}{}^2}$$

$$\approx -2DL^2\, e^{-2D_r t} \sqrt{\frac{3}{4\pi}} < \hat{u}_{z1} >_0 \sqrt{1 - < \hat{u}_{z1} >_0^2}$$

Since the average $\left\langle \cdots \right\rangle_0$ refers to free diffusion (just like the pdf $P^{(0)}$), we have, according to eqn. (2.141)

$$\left\langle \hat{u}_{z1} \right\rangle_0 = e^{-2D_r t}$$

and therefore

$$\gamma_{10}\left(t\right) \approx -2DL^2 \sqrt{\frac{3}{4\pi}}\; e^{-4D_r t} \sqrt{1 - e^{-4D_r t}}$$

We thus obtain the following mean-field result for the orientation

$$\left\langle \hat{u}_{z1} \right\rangle(t) = \mathrm{e}^{-2D_r t} \left[1 - 2DL^2\, \bar{\rho} D_r \sqrt{\frac{3}{4\pi}} \int_0^t dt'\, e^{-2D_r t'} \sqrt{1 - e^{-4D_r t'}} \right]$$

Introducing the new integration variable $x = D_r t'$ this gives

$$\left\langle \hat{u}_{z1} \right\rangle (t) = \mathrm{e}^{-2D_r t} \left[1 - C \int_0^{D_r t} dx\, e^{-4x} \sqrt{1 - e^{-4x}} \right]$$

with

$$C = 2DL^2 \sqrt{\frac{3}{4\pi}} \overline{\rho} = \frac{8}{\pi} \sqrt{\frac{3}{4\pi}} \frac{L}{D} \varphi$$

where $\varphi = \frac{\pi}{4} D^2 L \overline{\rho}$ is the volume fraction of rods. Finally, introducing the function

$$G(z) = -\frac{8}{\pi} \sqrt{\frac{3}{4\pi}}\, e^{-2z} \int_0^z dx\, e^{-2x} \sqrt{1 - e^{-4x}}$$

the average orientation can be written as

$$\left\langle \hat{u}_{z1}(t) \right\rangle = \left(\mathrm{e}^{-2D_r t} + \frac{L}{D} \varphi\, G(D_r t) \right)$$

Since $G<0$, orientational relaxation is faster for higher concentrations. This is due to the repelling interactions between rods (note that the expression for the torque that we used is valid for hard-core interactions).

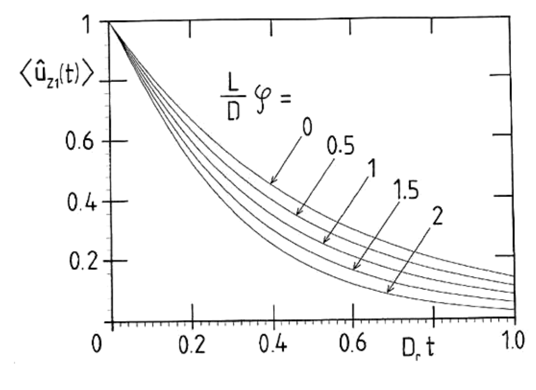


Fig. 6.24: The *z*-component of the average orientation as a function of time.

Exercise Chapter 7: SEDIMENTATION

7.1 The deviatoric part of the force that the fluid exerts per unit area on the surface of a translating sphere in an unbounded incompressible fluid is equal to (see eqn.(5.6))

$$\vec{f}^{\,dev} = \eta_0 \left\{ \nabla \vec{u}_0(\vec{r}) + \left[\nabla \vec{u}_0(\vec{r}) \right]^T \right\} \cdot \hat{r}$$

The fluid flow velocity is given in eqn. (7.19)

$$\vec{u}_0(\vec{r}\,') = \left\{ \frac{3}{4}\frac{a}{r'}\left[\hat{I} + \frac{\vec{r}\,'\vec{r}\,'}{r'^2} \right] + \frac{1}{4}\left(\frac{a}{r'}\right)^3 \left[\hat{I} - 3\frac{\vec{r}\,'\vec{r}\,'}{r'^2} \right] \right\} \cdot (\vec{v}_S - \vec{u}_S)$$

First we show that

$$\vec{f}^{\,dev}(\vec{r}) = -\frac{3\eta_0}{2a}\left[\hat{I} - \hat{r}\hat{r} \right] \cdot (\vec{v}_S - \vec{u}_S)$$

According to the above expression for $\vec{u}_0$, there are four different contributions

$$\sim \frac{1}{r}, \frac{\vec{r}\,\vec{r}}{r^3}, \frac{1}{r^3}, \frac{\vec{r}\,\vec{r}}{r^5}$$

A little effort shows that

$$\boxed{\begin{aligned}
&\nabla_i \frac{1}{r} = -\frac{r_i}{r^3}\\
&\nabla_i \frac{\vec{r}\,\vec{r}}{r^3} = -3\frac{r_i\,r_n\,r_m}{r^5} + \frac{\delta_{in}r_m + \delta_{im}r_n}{r^3}\\
&\nabla_i \frac{1}{r^3} = -3\frac{r_i}{r^5}\\
&\nabla_i \frac{\vec{r}\,\vec{r}}{r^5} = -5\frac{r_i\,r_n\,r_m}{r^7} + \frac{\delta_{in}r_m + \delta_{im}r_n}{r^5}
\end{aligned}}$$

Hence

$$\nabla_i\, \vec{u}_{0,n}\left(\vec{r}\right) = \left\{ \begin{aligned} &\frac{3a}{4}\left[-\frac{r_i}{r^3}\delta_{nm} - 3\frac{r_i\,r_n\,r_m}{r^5} + \frac{\delta_{in}r_m + \delta_{im}r_n}{r^3} \right] \\ &+\frac{a^3}{4}\left[-3\frac{r_i}{r^5}\delta_{nm} + 15\frac{r_i\,r_n\,r_m}{r^7} - 3\,\frac{\delta_{in}r_m + \delta_{im}r_n}{r^5} \right] \end{aligned} \right\} \cdot \left(\vec{v}_s - \vec{u}_s\right)_m$$

which reduces for $r = a$ to (summation over repeated indices is assumed here)

$$\nabla_i\, \vec{u}_{0,n}\left(\vec{r}\right) = \frac{3}{2a}\left[-\frac{r_i}{a}\delta_{nm} + \frac{r_i\,r_n\,r_m}{a^3} \right]\left(\vec{v}_s - \vec{u}_s\right)_m$$

The deviatoric part of the force is thus equal to

$$\begin{aligned}
\vec{f}^{\,dev} &= \eta_0 \left\{ \nabla \vec{u}_0\left(\vec{r}\right) + \left[\nabla \vec{u}_0\left(\vec{r}\right)\right]^T \right\} \cdot \frac{\vec{r}}{a} \\
&= \frac{3\eta_0}{2a}\left[-\hat{I} + \frac{\vec{r}\,\vec{r}}{a^2} \right] \cdot \left(\vec{v}_s - \vec{u}_s\right)
\end{aligned}$$

This expression can be integrated over the angles, that is, over the surface of the sphere, using that

$$\oint_{\partial V_0} dS\, \hat{I} = 4\pi a^2 \hat{I} \quad \text{and} \quad \oint_{\partial V_0} dS\, \hat{r}\,\hat{r} = \frac{4\pi}{3} a^2 \hat{I}$$

from which it follows that

$$\oint_{\partial V^0} dS\, \vec{f}^{\,dev}(\vec{r}) = -4\pi\eta_0 a\left(\vec{v}_S - \vec{u}_S\right)$$

7.2 Sedimentation of "sticky spheres"

An attractive potential between colloids will change the average distance between them, and thereby the sedimentation coefficient. In this exercise we consider the effect of an additional, short-ranged attractive "square-well" interaction potential

$$V^{+}(r)=\begin{cases} 0, & 0\le r\le 2a \\ -\varepsilon, & 2a<r<2a+\Delta \\ 0, & r\ge 2a+\Delta \end{cases}$$

where ε is the depth of the square well and Δ is its width. This potential is in addition to the usual hard core interaction potential. For this attractive potential plus the hard-core potential, we have

$$g(ax)=\begin{cases} 0, & x\le 2 \\ e^{\beta\varepsilon}, & 2<x<2+\dfrac{\Delta}{a} \\ 1, & x\ge 2+\dfrac{\Delta}{a} \end{cases}$$

From eqns. (7.33-35)

$$\vec{V}\,'=3\varphi\vec{v}_S^{\,0}\int_{x>1} dx\,x\left[g(ax)-1\right]=3\varphi\vec{v}_S^{\,0}\left\{-\int_1^2 dx\,x+\int_2^{2+\frac{\Delta}{a}} x\left(e^{\beta\varepsilon}-1\right)\right\}$$

$$=-\frac{9}{2}\varphi\vec{v}_S^{\,0}+\frac{3}{2}\varphi\vec{v}_S^{\,0}\left(e^{\beta\varepsilon}-1\right)\left[\left(2+\frac{\Delta}{a}\right)^2-4\right]$$

and

$$\vec{W}=\left(\sum_{j=1}^{N}\left\langle\Delta\vec{D}_{1j}\right\rangle\right)\cdot\beta\vec{F}^{ext}$$

$$=\varphi\vec{v}_S^{\,0}\left(e^{\beta\varepsilon}-1\right)\left[\frac{15}{4}\left(2+\frac{\Delta}{a}\right)^{-1}-\frac{9}{8}\left(2+\frac{\Delta}{a}\right)^{-3}-\frac{75}{16}\left(2+\frac{\Delta}{a}\right)^{-4}\right]$$

$$+\varphi\vec{v}_S^{\,0}e^{\beta\varepsilon}\left[-\frac{15}{8}+\frac{9}{72}+\frac{75}{256}\right]$$

while $\vec{V}\,''=(1/2)\varphi\vec{v}_S^{\,0}$ remains unaltered. Here we used the Rodne-Prager approximation (see eqn.(7.12)) for the mobility functions. Hence, from eqn.(7.32), using that $\vec{u}_S = -\varphi \vec{v}_S^{\,0}$

$$\begin{aligned}
\vec{v}_S &= \vec{u}_S + \vec{v}_S^{\,0} + \vec{V}' + \vec{V}'' + \vec{W} + O\left(\varphi^2\right) \\
&= \vec{v}_S^{\,0} - 6.44\varphi \vec{v}_S^{\,0} \\
&\quad + \varphi \vec{v}_S^{\,0}\left(e^{\beta\varepsilon} - 1\right)\left[-7.44 + \frac{3}{2}\left(2+\frac{\Delta}{a}\right)^2 + \frac{15}{4}\left(2+\frac{\Delta}{a}\right)^{-1} - \frac{9}{8}\left(2+\frac{\Delta}{a}\right)^{-3} - \frac{75}{16}\left(2+\frac{\Delta}{a}\right)^{-4}\right]
\end{aligned}$$

Defining the "stickiness parameter"

$$\boxed{\alpha = \lim_{\substack{\varepsilon\to\infty \\ \Delta\to 0}}\left(e^{\beta\varepsilon}-1\right)\left[\left(2+\frac{\Delta}{a}\right)^3 - 8\right] = 12\lim_{\substack{\varepsilon\to\infty \\ \Delta\to 0}}\left(e^{\beta\varepsilon}-1\right)\frac{\Delta}{a}}$$

we can now take the corresponding "sticky-sphere" limit,

$$\begin{aligned}
f(\varepsilon,\Delta) &= \left(e^{\beta\varepsilon}-1\right)\left[-7.441 + \frac{3}{2}\left(2+\frac{\Delta}{a}\right)^2 + \frac{15}{4}\left(2+\frac{\Delta}{a}\right)^{-1} - \frac{27}{24}\left(2+\frac{\Delta}{a}\right)^{-3} - \frac{75}{16}\left(2+\frac{\Delta}{a}\right)^{-4}\right] \\
&= \left(e^{\beta\varepsilon}-1\right)\left[-7.441 + 6\left(1+\frac{\Delta}{a}\right) + \frac{15}{8}\left(1-\frac{\Delta}{2a}\right) - \frac{27}{192}\left(1-3\frac{\Delta}{2a}\right) - \frac{75}{256}\left(1-2\frac{\Delta}{a}\right)\right] \\
&= \frac{\Delta}{a}\left(e^{\beta\varepsilon}-1\right)\left[6 - \frac{15}{16} + \frac{27}{128} + \frac{75}{128}\right] \approx 5.856\frac{\Delta}{a}\left(e^{\beta\varepsilon}-1\right)
\end{aligned}$$

and hence

$$\boxed{\vec{v}_S = \vec{v}_S^{\,0}\left[1 - \left(6.44 - 0.488\,\alpha\right)\varphi\right]}$$

Note that attractions lead to an enhancement of sedimentation. This is due to the fact that the particles are on average closer to each other. Each of the two particles "drags" the other one along through hydrodynamic interactions

7.3 Sedimentation of superparamagnetic particles

Here we consider spherical Brownian particles with a magnetic moment. In general the anisotropy of the magnetic interaction results in a non-zero torque on the core, which is mediated via the magnetic dipole moment. In case of superparamagnetic particles, however, where the magnetic dipole can frictionless rotate relative to the core-material, the torque acting on the core of each particle is zero. Superparamagnetic Brownian particles thus remain torque free. This implies that the hydrodynamic interaction functions are the same as for colloids with spherically-symmetric interactions.

For the calculation of the sedimentation velocity of Brownian particles carrying a superparamagnetic core, the pair-correlation function is

$$g\left(\vec{r},\hat{u}_1,\hat{u}_2\right)=g_{hs}\left(r\right)\exp\left(-\beta V\left(\vec{r},\hat{u}_1,\hat{u}_2\right)\right)$$

where $g_{hs}\left(r\right)$ is the hard-sphere pair-correlation function, and $V\left(\vec{r},\hat{u}_1,\hat{u}_2\right)$ is the pair-potential of two magnetic dipoles $\vec{m}_1=m\hat{u}_1,\quad \vec{m}_2=m\hat{u}_2$

$$V\left(\vec{r},\hat{u}_1,\hat{u}_2\right)=\frac{m^2\mu_0}{4\pi}\frac{\hat{u}_1\cdot\hat{u}_2-3\left(\hat{r}\cdot\hat{u}_1\right)\left(\hat{r}\cdot\hat{u}_2\right)}{r^3},\quad r\geq 2a$$

We first verify that eqns.(7.32- 35) for the sedimentation velocity remains valid, except that the pair-correlation function is now replaced by

$$g\left(r\right)=\frac{1}{\left(4\pi\right)^2}\oint d\hat{u}_1\oint d\hat{u}_2\, g\left(\vec{r},\hat{u}_1,\hat{u}_2\right)$$

In fact, this follows from the observation that the hydrodynamic functions are only functions of the distances between the spheres (no orientation of the dipoles are involved). Averaging over all degrees of freedom, also involving orientations, immediately leads to our original equations with the above expression for the correlation function.

Note that for permanent dipoles that couple mechanically to the cores of the Brownian spheres, the hydrodynamic interaction functions are different, also involving the orientations of the dipoles. For these systems the analysis below cannot be made.

For sufficiently weak magnetic interactions we can Taylor expand the

the Boltzmann exponent, leading to

$$g(r) = g_{hs}(r)\frac{1}{(4\pi)^2}\oint d\hat{u}_1 \oint d\hat{u}_2 \left[1-\beta V(\vec{r},\hat{u}_1,\hat{u}_2)+\frac{1}{2}\beta^2 V^2(\vec{r},\hat{u}_1,\hat{u}_2)\right]$$

$$= g_{hs}(r)\left[1+\frac{\beta^2}{2(4\pi)^2}\oint d\hat{u}_1 \oint d\hat{u}_2\, V^2(\vec{r},\hat{u}_1,\hat{u}_2)\right]$$

$$= g_{hs}(r)\left\{\begin{array}{l} 1+\left[\dfrac{\beta^2}{2(4\pi)^2}\left[\left(\dfrac{m^2\mu_0}{4\pi}\right)^2\dfrac{1}{r^6}\right]\oint d\hat{u}_1 \oint d\hat{u}_2\right. \\ \qquad \times\left\{\hat{u}_1\hat{u}_1 : \hat{u}_2\hat{u}_2 + 9(\hat{r}\hat{r}:\hat{u}_1\hat{u}_1)(\hat{r}\hat{r}:\hat{u}_2\hat{u}_2) - 6\hat{r}\cdot(\hat{u}_1\hat{u}_1)\cdot(\hat{u}_2\hat{u}_2)\cdot\hat{r}\right\}\end{array}\right\}$$

Note that from symmetry

$$\oint d\hat{u}_1 \oint d\hat{u}_2\, V(\vec{r},\hat{u}_1,\hat{u}_2) = 0$$

Now using that

$$\oint d\hat{u}\, \hat{u}\hat{u} = \frac{4\pi}{3}\hat{I}$$

the angular integrations can be done, giving

$$g(r) = g_{hs}(r)\left\{1+\frac{\beta^2}{2}\left[\left(\frac{m^2\mu_0}{4\pi}\right)^2\frac{1}{r^6}\right]\times\left\{\frac{1}{9}\hat{I}:\hat{I}+(\hat{r}\hat{r}:\hat{I})(\hat{r}\hat{r}:\hat{I})-\frac{2}{3}\hat{r}\cdot(\hat{I})\cdot(\hat{I})\cdot\hat{r}\right\}\right\}$$

$$= g_{hs}(r)\left\{1+\frac{\beta^2}{2}\left[\left(\frac{m^2\mu_0}{4\pi}\right)^2\frac{1}{r^6}\right]\times\left\{\frac{1}{3}+1-\frac{2}{3}\right\}\right\}$$

$$= g_{hs}(r)\left\{1+\frac{\beta^2}{3}\left[\left(\frac{m^2\mu_0}{4\pi}\right)^2\frac{1}{r^6}\right]\right\}$$

This expression for the pair-correlation function can now be substituted into eqns. (7.32-35), that is,

$$\vec{V}\,' = 3\varphi\vec{v}_S^{\,0}\int_{x>1} dx\, x\left[g(ax)-1\right],$$

$$\vec{V}\,'' = \frac{1}{2}\varphi\vec{v}_S^{\,0},$$

$$\vec{W} = \varphi\vec{v}_S^{\,0}\int_0^\infty dx\, x^2 g(ax)\left[\Delta A_S(ax)+\Delta A_C(ax)+2\Delta B_S(ax)+2\Delta B_C(ax)\right]$$

to obtain the following expressions for the two non-trivial contribution to the sedimentation velocity, with the abbreviation $\alpha \equiv \beta^2 m^4 \mu^2{}_0 / 48\pi^2$

$$\vec{V}\,' = 3\varphi\,\vec{v}_S^0 \int\limits_{x>1} dx\, x\left[g\left(ax\right)-1\right] = -3\varphi\,\vec{v}_S^0 \int\limits_1^2 dx\, x + 3\varphi\,\vec{v}_S^0 \frac{\alpha}{a^6}\int\limits_2^\infty dx\, x\frac{1}{x^6}$$
$$= -\frac{9}{2}\varphi\,\vec{v}_S^0 + \frac{3}{64}\varphi\,\vec{v}_S^0\frac{\alpha}{a^6} = -\frac{9}{2}\varphi\,\vec{v}_S^0 + \varphi\,\vec{v}_S^0\left(\frac{\beta\, m^2\mu_0}{32\,\pi\, a^3}\right)^2$$

and

$$\vec{W} = \varphi\,\vec{v}_S^0\int\limits_0^\infty dx\, x^2 g\left(ax\right)\left[\Delta A_S\left(ax\right)+\Delta A_C\left(ax\right)+2\Delta B_S\left(ax\right)+2\Delta B_C\left(ax\right)\right]$$
$$= \varphi\,\vec{v}_S^0\int\limits_2^\infty dx\, x^2\left[1+\frac{\alpha}{x^6 a^6}\right]\times\left\{-\frac{15}{4}x^{-4}+\frac{11}{2}x^{-6}+\frac{75}{4}x^{-7}-\frac{17}{8}x^{-6}\right\}$$
$$= \varphi\,\vec{v}_S^0\left[-1.44-0.04\left(\frac{\beta\, m^2\mu_0}{32\,\pi\, a^3}\right)^2\right]$$

The sedimentation velocity is thus found to be equal to

$$\boxed{\begin{aligned}\vec{v}_S &= \left(1-\varphi\right)\vec{v}_S^0 + \vec{V}\,' + \vec{V}\,'' + \vec{W} + O\left(\varphi^2\right)\\ &= \vec{v}_S^0\left[1+\left(-6.44+0.96\left(\frac{\beta m^2\mu_0}{32\pi a^3}\right)^2\right)\varphi\right]\end{aligned}}$$

The dipoles will on average align such that they attract each other (since this decreases the interaction energy), which leads to smaller distances between the spheres, which in turn leads to a faster sedimentation ("pairs" sediment faster as "singlets"), just like for the sticky spheres in the previous exercise.

The above analysis is valid up to a leading order expansion in the interaction-strength parameter

$$z \equiv \frac{\beta m^2\mu_0}{32\pi a^3}$$

For larger values of this parameter, we need to retain the full Boltzmann exponent in the expression for the pair-correlation function

$$g(r) = \frac{g_{hs}(r)}{\left(4\pi\right)^2}\oint d\hat{u}_1\oint d\hat{u}_2\, e^{-\beta V(\vec{r},\hat{u}_1,\hat{u}_2)}$$

The four-fold integration (with respective to $\hat{u}_1$ and $\hat{u}_2$) can be reduced to a three-fold integral as follows. Without loss of the generality, $\hat{r}$ can be chosen along the *z*-axis. The orientations can now be written in spherical coordinates

$$\hat{u}_1 = \left(\sin\theta_1 \cos\phi_1, \sin\theta_1 \sin\phi_1, \cos\theta_1\right)$$
$$\hat{u}_2 = \left(\sin\theta_2 \cos\phi_2, \sin\theta_2 \sin\phi_2, \cos\theta_2\right)$$

where θ_i is the angle of $\hat{u}_i$ with the z-axis, and ϕ_i is the azimuthal angle. Thus

$$\begin{aligned}\hat{u}_1 \cdot \hat{u}_2 &= \sin\theta_1 \sin\theta_2 \left[\cos\phi_1 \cos\phi_2 + \sin\phi_1 \sin\phi_2\right] + \cos\theta_1 \cos\theta_2 \\ &= \sin\theta_1 \sin\theta_2 \cos\left(\phi_1 - \phi_2\right) + \cos\theta_1 \cos\theta_2\end{aligned}$$

Therefore

$$\begin{aligned}g(r) = \frac{g_{hs}(r)}{(4\pi)^2} \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_{-1}^{1} d\left(\cos\theta_1\right) \int_{-1}^{1} d\left(\cos\theta_2\right) \\ \times \exp\left\{-Z\left[\sqrt{1-\cos^2\theta_1}\sqrt{1-\cos^2\theta_2}\cos\left(\phi_1-\phi_2\right) - 2\cos\theta_1\cos\theta_2\right]\right\}\end{aligned}$$

where

$$Z \equiv \left(\frac{\beta m^2 \mu_0}{32\pi a^3}\right)\left(\frac{2a}{r}\right)^3$$

Introducing the new integration variables

$$\Phi = \left(\phi_1 - \phi_2\right), \quad x_1 = \cos\theta_1, \quad x_2 = \cos\theta_2$$

this gives

$$g(r) = \frac{g_{hs}(r)}{8\pi} \int_0^{2\pi} d\Phi \int_{-1}^{1} dx_1 \int_{-1}^{1} dx_2 \exp\left\{-Z\left[\sqrt{1-x_1^2}\sqrt{1-x_2^2}\cos\Phi - 2x_1x_2\right]\right\}$$

Repeating the calculation of the sedimentation coefficient, just like for the small interaction parameter, we get

$$\vec{v}_s = \vec{v}_S^{\,0}\left[1 + \left(-6.441 + f\left(\frac{\beta m^2 \mu_0}{32\pi a^3}\right)\right)\varphi + O\left(\varphi^2\right)\right]$$

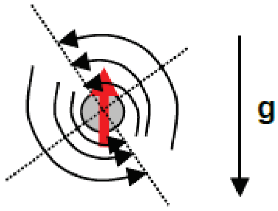
where *f* represents the integrals encountered in the expressions 7.32-35, with a pair-correlation function equal to

$$g(r) = g_{hs}\left(r\right) G\left(\frac{\beta m^2 \mu_0}{32\pi a^3}\left(\frac{2a}{r}\right)^3\right)$$
$$G\left(Z\right) = \frac{1}{8\pi} \int_0^{2\pi} d\Phi \int_{-1}^{1} dx_1 \int_{-1}^{1} dx_2 \exp\left\{-Z\left(\sqrt{1-x_1^2}\sqrt{1-x_2^2}\cos\varphi - 2\,x_1\,x_2\right)\right\}$$

which is used for the numerical calculations of the sedimentation coefficient in Fig. 7.9.

7.4 Superparamagentic particles in an external magnetic field

Let us now consider the sedimentation velocity in the presence of an external homogeneous magnetic field, which does not exert a force, but only exerts a torque, and tends to align the magnetic dipoles.



In case of a strong magnetic field (in the *z*-direction), the dipoles are perfectly aligned so that the pair-correlation function is equal to

$$g(\vec{r}) = g_{hs}(r)\exp\left(-\frac{\beta m^2 \mu_0}{4\pi}\frac{1-3\hat{r}_z^2}{r^3}\right)$$

where $\hat{r}_z$ is the *z*-component of the distance $\vec{r}$ between the centers of two particles. This follows from the interaction potential given at the beginning of the previous exercise, with both dipole orientations along the *z*-direction.

Contrary to the case without an external field, the pair-correlation function is anisotropic, that is, it depends on the direction of $\vec{r}$. The spherical-angular integrations with respect to $\vec{r}$ in the expressions for

$$\vec{V}' = \bar{\rho}\int_{r>a} d\vec{r}\left[g(r)-1\right]\vec{u}_0(\vec{r}),$$

$$\vec{V}'' = \frac{1}{6}a^2\bar{\rho}\int_{r>a} d\vec{r}\left[g(r)-1\right]\nabla_r^2\vec{u}_0(\vec{r}) + \frac{1}{2}\varphi\vec{v}_S^{\,0},$$

$$\vec{W} = \left(\sum_{j=1}^{N}\left\langle \Delta\vec{D}_{1j}\right\rangle\right)\cdot\beta\vec{F}^{ext}$$

$$= \bar{\rho}\int d\vec{r}\, g(\vec{r})\left\{\begin{array}{l}\left[\Delta A_S(r)+\Delta A_C(r)-\Delta B_S(r)-\Delta B_C(r)\right]\hat{r}\hat{r} \\ +\left[\Delta B_S(r)+\Delta B_C(r)\right]\hat{I}\end{array}\right\}\cdot\beta\vec{F}^{ext}$$

must now be done explicitly. These integrations can be evaluated analytically for weak magnetic interactions, where $\beta m^2\mu_0/32\pi a^3 < 1$. The pair-correlation function is then approximately equal to

$$g(\vec{r}) \approx g_{hs}(r)\left[1-\frac{\beta m^2\mu_0}{4\pi}\frac{1-3\hat{r}_z^2}{r^3}\right] \qquad (1)$$

The mathematical identities (where the integrals range over all orientations, that is, the two spherical-angular coordinates of $\vec{r}$)

$$\begin{aligned} &\oint d\hat{r}\left(1-3\hat{r}_z^2\right)=0 \\ &\oint d\hat{r}\left(1-3\hat{r}_z^2\right)\hat{r}\hat{r}=\frac{16\pi}{15}\begin{pmatrix}1/2 & 0 & 0\\ 0 & 1/2 & 0\\ 0 & 0 & -1\end{pmatrix}\end{aligned} \tag{2}$$

can be proven by using that

$$\hat{r}=\left(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta\right)$$

where θ and ϕ are the spherical-angular coordinates, which vary within the intervals $0\le\theta<\pi,\quad 0\le\phi<2\pi$, while the integral over all orientations in terms of these coordinates is equal to

$$\oint d\hat{r}(\cdots)=\int_0^{\pi}d\theta\sin\theta\int_0^{2\pi}d\phi(\cdots)$$

The evaluation of $\vec{V}'$, $\vec{V}''$, and $\vec{W}$ can now be done to first order in the volume fraction, using $\vec{u}_s=-\varphi\,\vec{v}_S^0$ (in eqn. (7.19)), and the expressions in eqn.(7.12) for the hydrodynamic functions $\Delta A_{S,C}(r)$ and $\Delta B_{S,C}(r,)$ and noting that $\vec{F}^{ext}=6\pi\eta_0\vec{v}_S^0$.

This is a long but straightforward calculation (with the use of the identities eqn. (2)), and leads to

$$\vec{v}_S=\left[\left(1-6.44\,\varphi\right)\hat{I}-1.87\,\varphi\frac{\beta m^2\mu_0}{32\pi a^3}\begin{pmatrix}1/2 & 0 & 0\\ 0 & 1/2 & 0\\ 0 & 0 & -1\end{pmatrix}\right]\cdot\vec{v}_S^0 \tag{3}$$

Note that there is a typo in the Jan's book (pp. 486): the " $\vec{v}_S^0$ " on the left side should be " $\vec{v}_S$ ". Eqn, (3) is for a magnetic field in the z-direction, while the direction of the gravitational force is along $\vec{v}_S^0$.

The above result can be generalized to an arbitrary direction of the magnetic field $\hat{B}$ as follows. First note that,

$$\begin{pmatrix}1/2 & 0 & 0\\ 0 & 1/2 & 0\\ 0 & 0 & -1\end{pmatrix}\cdot\vec{v}_S^0=\frac{1}{2}\begin{pmatrix}v_{S,x}\\ v_{S,y}\\ 0\end{pmatrix}-\begin{pmatrix}0\\ 0\\ v_{S,z}\end{pmatrix}$$

with $v_{S,x}$ the component of $\vec{v}_S^0$ in the x-direction, and similar for $v_{S,y}$ and $v_{S,z}$.

Since $\hat{B}$ was chosen along the z-direction, we can replace

$$\begin{pmatrix} 0 \\ 0 \\ v_{S,z} \end{pmatrix} = \hat{B}\hat{B}\cdot\vec{v}_S^{\,0} \quad \text{and} \quad \begin{pmatrix} v_{S,x} \\ v_{S,y} \\ 0 \end{pmatrix} = \left[\hat{I}-\hat{B}\hat{B}\right]\cdot\vec{v}_S^{\,0}$$

Then we have

$$\begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}\cdot\vec{v}_S^{\,0} = \frac{1}{2}\left[\hat{I}-\hat{B}\hat{B}\right]\cdot\vec{v}_S^{\,0} - \hat{B}\hat{B}\cdot\vec{v}_S^{\,0} = \frac{1}{2}\vec{v}_S^{\,0} - \frac{3}{2}\hat{B}\hat{B}\cdot\vec{v}_S^{\,0}$$

and therefore

$$\boxed{\vec{v}_S = \left[1-6.44\,\varphi - 0.93\,\varphi\,\frac{\beta m^2\mu_0}{32\pi a^3}\right]\cdot\vec{v}_S^{\,0} + 2.80\,\varphi\,\frac{\beta m^2\mu_0}{32\pi a^3}\left(\hat{B}\cdot\vec{v}_S^{\,0}\right)\hat{B}}$$

There are two special cases where $\hat{B} \parallel \vec{v}_S^{\,0}$ and $\hat{B}\perp\vec{v}_S^{\,0}$, that is, the magnetic field is along, and the perpendicular to the gravitational force, respectively.

From the above result it is found that the corresponding sedimentation velocities are equal to

$$\boxed{\begin{aligned} \vec{v}_{S,\parallel} &= \left[1-6.44\,\varphi + 1.87\,\varphi\,\frac{\beta m^2\mu_0}{32\pi a^3}\right]\vec{v}_S^{\,0} \\ \vec{v}_{S,\perp} &= \left[1-6.44\,\varphi - 0.93\,\varphi\,\frac{\beta m^2\mu_0}{32\pi a^3}\right]\vec{v}_S^{\,0} \end{aligned}}$$

Thus, for the case of $\hat{B} \parallel \vec{v}_S^{\,0}$ sedimentation is enhanced, while for the case of $\hat{B}\perp\vec{v}_S^{\,0}$ sedimentation is reduced.

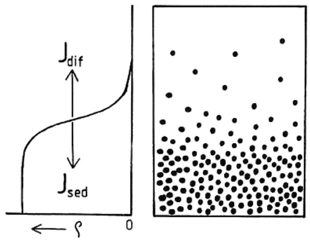
7.5 Relation between the hydrodynamic mobility function and sedimentation

In a steady state where diffusion sedimentation equilibrium is reached, we have

$$\vec{J}_{dif} + \vec{J}_{sed} = \vec{0}$$

From eqns. (7.79+81) for the two fluxes $\vec{J}_{dif} = -D_\nabla \nabla\rho$ and $\vec{J}_{sed} = M\rho\,\vec{F}^{ext}$, it follows that

$$D_\nabla \nabla\rho = M\,\rho\,\vec{F}^{ext}$$



The external force can be eliminated using eqn. (7.70), to obtain

$$D_\nabla \nabla\rho = M\,\rho\left[\nabla_r \ln\rho(\vec{r},t)\right]\frac{d\Pi\left(\rho(\vec{r})\right)}{d\rho(\vec{r})}$$

and hence

$$D_\nabla = M\frac{d\Pi\left(\rho(\vec{r})\right)}{d\rho(\vec{r})} = M\frac{k_BT}{S(k\to 0)}$$

Identifying $D_\nabla = D_c^S(k\to 0)$ (see chapter 6), and using eqn. (6.94), this leads to

$$D_\nabla = D_0\frac{H(k\to 0)}{S(k\to 0)} = M\frac{k_BT}{S(k\to 0)}$$

The mobility is thus equal to

$$M = (k_BT)^{-1}\,D_0H(k\to 0) = \frac{H(k\to 0)}{6\pi\eta_0 a} = \beta D_0 H(k\to 0)$$

The numerator in eqn. (6.92) is nothing but $H(k\to 0) = 1 - 6.44\varphi + \mathrm{O}(\varphi^2)$, and hence

$$\boxed{M = \beta D_0\left[1 - 6.44\varphi\right]}$$

Since the sedimentation flux is related to the sedimentation velocity as

$$\vec{J}_{sed} = \rho\,\vec{v}_s = M\rho\vec{F}^{ext}$$

so that

$$\vec{v}_s = M\,\vec{F}^{ext}$$

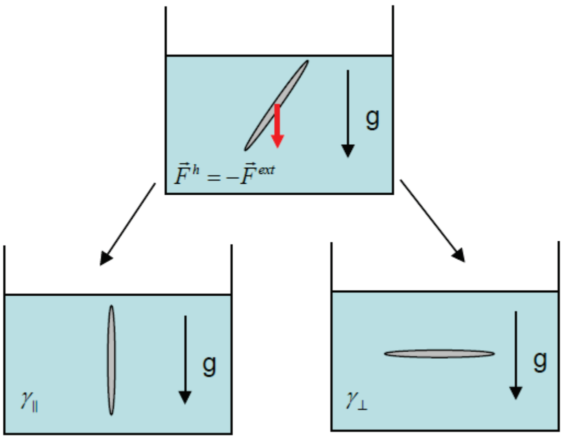
and

$$\vec{v}_s^{\,0} = \beta D_0\,\vec{F}^{ext}$$

we finally find the sedimentation velocity is as $\vec{v}_s = \vec{v}_s^{\,0}\left[1 - 6.44\varphi\right]$, which reproduces the expression (7.40), as it should.

7.6 Do rods align during sedimentation?

Since the translational friction coefficient of a rod depends on its orientation, one may ask whether a rod will align during sedimentation. This question will be answered in this exercise. When there is a torque, the two possible stationary orientations are either of the two given in the figure below. As we will see, however, there is no torque, so that the rod remains in its original orientation. The sedimentation velocity, however, is not co-linear with the external force.



Since the creeping-flow equations (together with the boundary conditions) are linear, the sedimentation velocity is the sum of $\vec{v}^{\,0}_{S,\parallel}$ and $\vec{v}^{\,0}_{S,\perp}$, where $\vec{v}^{\,0}_{S,\parallel}$ is the velocity due to the force $\vec{F}_\parallel$ parallel to the rod's long axis, and where $\vec{v}^{\,0}_{S,\perp}$ is the velocity due to perpendicular force $\vec{F}_\perp$. The same holds for the hydrodynamic torque. The torque for an arbitrary orientation of the rod, can be decomposed in a torque $\vec{T}^h_\parallel$ due to the component of the sedimentation velocity along the long axis of the rod (see the left-lower figure), and torque $\vec{T}^h_\perp$, resulting from the perpendicular velocity component (see the right-lower figure). The torque for an arbitrary orientation is simply the sum of these two torques: $\vec{T}^h = \vec{T}^h_\parallel + \vec{T}^h_\perp$.

From symmetry, both of these torques are trivially equal to zero. Therefore the total torque, being the sum of them, is also zero. There is thus no rotation induced by sedimentation, provided that rods are not interacting with each other. Rod-rod interactions can lead to a finite torque, and therefore alignment can occur during sedimentation at finite concentrations.

From eqn. (5.120, 123,124), the velocity of rod with orientation $\hat{u}$ on which a force acts is equal to $\vec{F}^{ext} = -\vec{F}^h$

$$v_s^0 = \frac{-1}{3\pi\eta_0 L}\left\{ f_\parallel\left(\frac{L}{D}\right)\hat{u}\hat{u} + f_\perp\left(\frac{L}{D}\right)\left[\hat{I} - \hat{u}\hat{u}\right]\right\} \cdot \vec{F}^h \qquad (1)$$

where
$$f_{\|}\left(\frac{L}{D}\right)=\frac{3}{2}\ln\left(\frac{L}{D}\right),\quad f_{\perp}\left(\frac{L}{D}\right)=\frac{3}{4}\ln\left(\frac{L}{D}\right) \qquad (2)$$

Averaging over all orientations, using that
$$\langle\hat{u}\hat{u}\rangle=\frac{1}{4\pi}\oint d\hat{u}\,\hat{u}\hat{u}=\frac{1}{3}\hat{I}$$
where, as before, $\hat{I}$ is the identity matrix, leads to
$$\langle\vec{v}_S^0\rangle=\frac{1}{3\pi\eta_0 L}\ln\left(\frac{L}{D}\right)\vec{F}^{ext}$$

Note that the orientationally averaged parallel velocity is twice as large as the perpendicular velocity
$$\boxed{<\vec{v}_{S,\|}^0>=2<\vec{v}_{S,\perp}^0>}$$

It follows from eqn. (1) that when $\hat{u}\,//\,\vec{F}^{ext}$, for a fixed orientation, the sedimentation velocity is equal to
$$\vec{v}_{S,//}^0=\frac{1}{3\pi\eta_0 L}\left[\frac{1}{3}f_{\|}\left(\frac{L}{D}\right)\right]\vec{F}^{ext}=\frac{1}{2\pi\eta_0 L}\ln\left(\frac{L}{D}\right)\vec{F}^{ext}$$

while for $\hat{u}\perp\vec{F}^{ext}$ the velocity is equal to
$$\vec{v}_s^0=\frac{1}{3\pi\eta_0 L}\left[\frac{1}{3}f_{\perp}\left(\frac{L}{D}\right)\right]\vec{F}^{ext}=\frac{1}{4\pi\eta_0 L}\ln\left(\frac{L}{D}\right)\vec{F}^{ext}$$

For an arbitrary orientation the sedimentation velocity is not co-linear with the external force. Let $\vec{F}^{ext}=\hat{e}F^{ext}$, where $\hat{e}$ is the direction of the external force. Taking the inner product of both sides of eqn. (1) with $\hat{e}$ gives
$$\hat{e}\cdot\vec{v}_S^0=\frac{1}{3\pi\eta_0 L}\left\{(f_{\|}-f_{\perp})\cos^2\Theta+f_{\perp}\right\}F^{ext}$$

where Θ is the angle between $\hat{e}$ and $\hat{u}$. The magnitude of the sedimentation velocity is, according to eqn.(1), equal to
$$v_S^0=\frac{F^{ext}}{3\pi\eta_0 L}\sqrt{(f_{\|}^2-f_{\perp}^2)\cos^2\Theta+f_{\perp}^2}$$

It follows from the two above equations that the angle ϕ between the force and the sedimentation velocity is related to the angle Θ between the force and the orientation as
$$\boxed{\cos\phi=\frac{\hat{e}\cdot\vec{v}_S^0}{v_S^0}=\frac{(f_{\|}-f_{\perp})\cos^2\Theta+f_{\perp}}{\sqrt{(f_{\|}^2-f_{\perp}^2)\cos^2\Theta+f_{\perp}^2}}}$$

7.9 Instead of a homogeneous initial density profile (that is already discussed in Figure 7.8 in the main text for interacting particles in the section 7.5), let us consider the ***evolution of the density*** starting with a situation where non-interacting particles are concentrated in a very thin layer located at height of z_0.

The concentration within the layer is assumed to be a constant (in the *x*- and *y*-directions) and is modeled as an infinitely thin layer. Mathematically this is formulated as

$$\varphi(z,t=0)=C_0\,\delta(z-z_0)$$

where δ is the delta distribution and C_0 is formally equal to the thickness of the layer multiplied by the volume fraction in that layer.

For non-interacting particles, substitution of the mobility, $M(\bar{\rho})=1/6\pi\eta_0 a$, and the osmotic pressure $\Pi=\bar{\rho}\,k_B T$ into eqn. (7.82)

$$\begin{aligned}\frac{\partial}{\partial t}\rho(\vec{r},t)&=-\nabla_r\cdot\vec{J}(\vec{r},t)\\&=\nabla_r\cdot M(\rho(\vec{r},t))\left[-\rho(\vec{r},t)\vec{F}^{ext}+(\nabla_r\rho(\vec{r},t))\frac{d\Pi(\rho(\vec{r},t))}{d\rho(\vec{r})}\right]\end{aligned}$$

gives the following equation for the local volume fraction $\varphi=\frac{4\pi}{3}a^3\rho$

$$\boxed{\frac{\partial}{\partial t}\varphi(z,t)=D_0\frac{\partial}{\partial z}\left[\varphi(z,t)\,\beta\left|\vec{F}^{ext}\right|+\frac{\partial}{\partial z}\varphi(z,t)\right],\quad z>0} \tag{1}$$

Note that the external force acts in the *minus z*-direction, so that the corresponding minus sign in eqn.(7.82) becomes a plus sign. The no-flux boundary condition at $z=0$ reads

$$\frac{\partial}{\partial t}\varphi(z,t)+\beta\left|\vec{F}^{ext}\right|\varphi(z,t)=0,\quad for\ z=0$$

In order to solve the differential equation (1), subject to the above formulated initial condition and boundary condition, we introduce the auxiliary function *u(z, t)*, defined as

$$\varphi(z,t)=u(z,t)\exp\left\{-\frac{\left|\vec{v}_S^{\,0}\right|}{2D_0}(z-z_0)-\frac{\left|\vec{v}_S^{\,0}\right|^2}{4D_0}t\right\}$$

Substitution of this definition into eqn. (1) trivially gives

$$\frac{\partial}{\partial t}u(z,t)=D_0\frac{\partial^2}{\partial z^2}u(z,t)$$

where it is used that

$$\left|\vec{v}_S^0\right|=\frac{1}{6\pi\eta_0 a}\left|\vec{F}^{ext}\right|$$

The initial and boundary conditions in terms of *u(z, t)* are

$$u(z,t=0)=C_0\,\delta(z-z_0), \tag{2}$$
$$D_0\frac{\partial}{\partial z}u(z,t)+\frac{1}{2}\left|\vec{v}_S^0\right|u(z,t)=0, \quad for \quad z=0 \tag{3}$$

The above diffusion equation for *u(z, t)* is formally identical to the 1-dimensional free diffusion equation. Solutions of this free-diffusion equation are

$$P_0(z\pm z_0,t)=\frac{C_0}{\sqrt{4\pi D_0 t}}\exp\left(-\frac{(z\pm z_0)^2}{4D_0 t}\right)$$

Note that there is a mistake in the Jan's book: $P_0(z,t)$ is in fact $P_0(z-z_0,t)$.

We will verify that the Ansatz

$$\begin{aligned}u(z,t)=&\,P_0(z-z_0,t)+P_0(z+z_0,t)\\&+\frac{\left|\vec{v}_S^0\right|}{D_0}\int_{z_0}^{\infty}dz'\,P_0(z+z',t)\exp\left\{\frac{\left|\vec{v}_S^0\right|}{2D_0}(z'-z_0)\right\}\end{aligned} \tag{4}$$

solves the three above equations. Since any linear combination of $P_0(z\pm z_0,t)$ solves the free diffusion equation, this expression for *u(z,t)* also solves that equation. We thus have to show that this Ansatz satisfies the initial condition (2) and the boundary condition (3).

Since

$$P_0(z\pm z_0,t=0)=C_0\,\delta(z\pm z_0)$$
$$P_0(z+z',t=0)=C_0\,\delta(z+z')$$

and $0\le z\le z_0$, it immediately follows that the initial condition (2) is satisfied.

Since for $z=0$

$$\frac{\partial}{\partial z}\left[P_0(z-z_0,t)+P_0(z+z_0,t)\right]=0$$

the boundary condition (3) is fulfilled when

$$\left|\vec{v}_S^0\right|\int_{z_0^+}^{\infty} dz'\frac{\partial}{\partial z'}P_0(z',t)\exp\left\{\frac{\left|\vec{v}_S^0\right|}{2D_0}\left(z'-z_0\right)\right\}$$
$$+\frac{1}{2}\left|\vec{v}_S^0\right|\left\{\frac{2C_0}{\sqrt{4\pi D_0 t}}\exp\left\{-\frac{z_0^2}{D_0 t}\right\}+\frac{\left|\vec{v}_S^0\right|}{D_0}C_0\int_{z_0}^{\infty}dz'\,P_0(z',t)\exp\left\{\frac{\left|\vec{v}_S^0\right|}{2D_0}\left(z'-z_0\right)\right\}\right\}=0$$

where we used that $\frac{\partial}{\partial z}P_0(z+z',t)$ for $z=0$ is equal to $\frac{\partial}{\partial z'}P_0(z',t)$.

A partial integration in the first integral leads directly to the verification of the boundary condition (3).

The volume fraction is thus found to be equal to

$$\varphi\left(z,t\right)=\left[P_0(z-z_0,t)+P_0(z+z_0,t)+\frac{\left|\vec{v}_S^0\right|}{D_0}C_0\int_{z_0}^{\infty}dz'\,P_0(z+z',t)\exp\left\{\frac{\left|\vec{v}_S^0\right|}{2D_0}\left(z'-z_0\right)\right\}\right]$$
$$*\exp\left\{-\frac{\left|\vec{v}_S^0\right|}{2D_0}\left(z-z_0\right)-\frac{\left|\vec{v}_S^0\right|^2}{4D_0}t\right\}$$

As a final step we introduce the integration variable

$$x=\frac{\left(z'+z\right)-\left|\vec{v}_S^0\right|t}{\sqrt{4D_0 t}}$$

which gives

$$\int_{z_0}^{\infty}dz'\,P_0(z+z',t)\exp\left\{\frac{\left|\vec{v}_S^0\right|}{2D_0}\left(z'-z_0\right)\right\}=$$
$$\frac{C_0}{\sqrt{\pi}}\exp\left\{\frac{\left|\vec{v}_S^0\right|^2 t}{4D_0}-\frac{(z+z_0)\left|\vec{v}_S^0\right|}{2D_0}\right\}\times\int_{\frac{z+z_0-\left|\vec{v}_S^0\right|t}{\sqrt{4D_0 t}}}^{\infty}dx\exp\left\{-x^2\right\}$$

Hence

$$\varphi(z,t)=\frac{C_0}{\sqrt{4\pi D_0 t}}\left\{\begin{array}{l}\exp\left(-\dfrac{(z-z_0)^2}{4D_0t}\right)\\ +\exp\left(-\dfrac{(z+z_0)^2}{4D_0t}\right)\end{array}\right\}\times\exp\left\{-\frac{\left|\vec{v}_S^{\,0}\right|}{2D_0}(z-z_0)-\frac{\left|\vec{v}_S^{\,0}\right|^2}{4D_0}t\right\}$$
$$+\frac{C_0}{\sqrt{\pi}}\frac{\left|\vec{v}_S^{\,0}\right|}{D_0}\exp\left(-\frac{\left|\vec{v}_S^{\,0}\right|}{D_0}z\right)\int_{\frac{z+z_0-\left|\vec{v}_S^{\,0}\right|t}{\sqrt{4D_0t}}}^{\infty}dx\exp\left\{-x^2\right\}$$

This density profile is plotted in Fig.7.10 (and re-plotted below). At small times, where the external force had no time to act, the profile is Gaussian, while at infinite time the barometric height distribution is attained.

Note : there is a typo in the book saying that $\left|\vec{v}_S^{\,0}\right|t/D_0\ll 1$, which should read $\left|\vec{v}_S^{\,0}\right|^2 t/D_0\ll 1$.

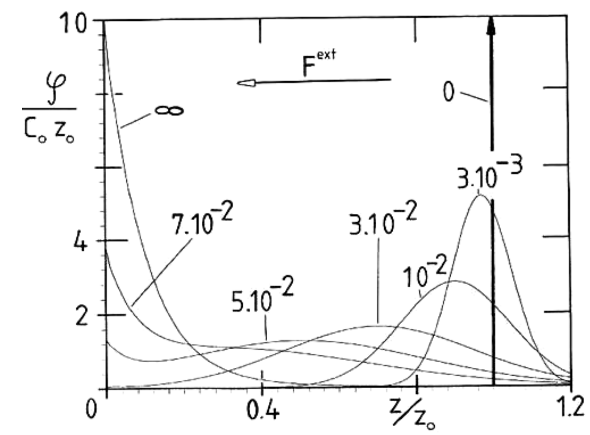


Fig. 7.10: Density profiles for non-interacting particles, initially centered in a thin layer at $z=z_0$. The plot $\dfrac{\varphi(z,t)}{C_0\,z_0}$ as a function of $\dfrac{z}{z_0}$ for various values of $\dfrac{D_0t}{z_0^2}$, which are indicated in the figure. Here, the value of $\dfrac{\left|\vec{v}_s^{\,0}\right|z_0}{D_0}=\dfrac{\left|\vec{F}^{ext}\right|z_0}{k_BT}$ is chosen equal to 10.

Exercise Chapter 8: CRITICAL PHENOMENA

Courtesy of St. Anton am Arlberg.com, Austria

8.1 Short-ranged character of the direct-correlation function

The Ornstein-Zernike equation for a homogeneous system reads

$$h(\vec{r}) = c(\vec{r}) + \rho \int d\vec{r}\,'\; c(\vec{r} - \vec{r}\,')\, h(\vec{r}\,')$$

where we introduced the new variables $\vec{r} = \vec{r}_1 - \vec{r}_2$ and $\vec{r}\,' = \vec{r}_3 - \vec{r}_2$. The integral is of a convolution type. Fourier transformation thus gives

$$h(k) = c(k) + \rho\, c(k) h(k)$$

and hence

$$\rho\, c(k) = \frac{\rho\, h(k)}{1 + \rho\, h(k)}$$

Note that $h(\vec{k}) \equiv h(k)$ for a homogeneous system. On approach of the critical point, $h(k \to 0) = \infty$, due to the long-ranged character of $h(\vec{r})$. From the above formula we thus have

$$\rho\, c(k \to 0) \approx 1$$

close to the critical point. The integral of $c(\vec{r})$ over $\vec{r}$ is therefore finite, contrary to the integral of $h(\vec{r})$. This reflects the short-ranged nature of the direct correlation function as compared to that of the total-correlation functions. This short-ranged nature of the direct correlation (as sketched in Fig.8.6), is used to analyze the critical behavior of the structure factor in the book.

8.2 Order of magnitude estimation of $\beta\Sigma / R_V^2$

Differentiating eqn. (8.33)

$$\Pi = \bar{\rho}\, k_B T - \frac{2\pi}{3}\bar{\rho}^2 \int_0^\infty dr'\, r'^3 \frac{dV(r')}{dr'} g(r')$$

with respect to the density leads to

$$\frac{d\Pi}{d\bar{\rho}} = k_B T - \frac{2\pi}{3}\int_0^\infty dr'\, r'^3 \frac{dV(r')}{dr'} \left\{ 2\bar{\rho} g(r') + \bar{\rho}^2 \frac{dg(r')}{d\bar{\rho}} \right\}$$

Near the critical point, where $\dfrac{d\Pi}{d\bar{\rho}} = 0$, this results in

$$\frac{4\pi}{3}\bar{\rho}\int_0^\infty dr'\, r'^3 \frac{dV(r')}{dr'} \left\{ g(r') + \frac{1}{2}\bar{\rho}\frac{dg(r')}{d\bar{\rho}} \right\} = k_B T \qquad (1)$$

For short-ranged attractions, superimposed on a hard-core potential, the derivative $\dfrac{dV(r')}{dr'}$ is concentrated around $r' \approx R_V$, so that $r'^3 \approx \dfrac{r'^5}{R_V^2}$ within the integral.
Replacing the factor $\dfrac{1}{2}$ in front of $\dfrac{dg(r')}{d\bar{\rho}}$ in the above equation, by $\dfrac{1}{8}$, the following (crude) estimate of Σ is obtained

$$\frac{\beta\Sigma}{R_V^2} = \beta\frac{2\pi}{15}\bar{\rho}\int_0^\infty dr' \left(\frac{r'^5}{R_V^2}\right)\frac{dV(r')}{dr'}\left\{ g(r') + \frac{1}{8}\bar{\rho}\frac{dg(r')}{d\bar{\rho}} \right\}$$
$$= \frac{\dfrac{2\pi}{15}\bar{\rho}\displaystyle\int_0^\infty dr' \left(\frac{r'^5}{R_V^2}\right)\frac{dV(r')}{dr'}\left\{ g(r') + \frac{1}{8}\bar{\rho}\frac{dg(r')}{d\bar{\rho}} \right\}}{\dfrac{4\pi}{3}\bar{\rho}\displaystyle\int_0^\infty dr' \left(\frac{r'^5}{R_V^2}\right)\frac{dV(r')}{dr'}\left\{ g(r') + \frac{1}{2}\bar{\rho}\frac{dg(r')}{d\bar{\rho}} \right\}} \simeq \frac{1}{10}$$

Thus

$$\boxed{\beta\Sigma / R_V^2 \approx 1/10}$$

Note that this estimate is also valid whenever $\dfrac{d\Pi}{d\bar{\rho}} \ll k_B T$, that is $\beta\dfrac{d\Pi}{d\bar{\rho}} \ll 1$

When this is the case, the two terms in the above expression for $\dfrac{d\Pi}{d\bar{\rho}}$ almost cancel, so that eqn. (1) is still valid.

8.3 Introducing the short-ranged contribution to the diffusion eqn. (8.45) gives,

$$0 = 2D_0 \nabla_r^{\ 2} \left[\beta \frac{d\Pi}{d\bar{\rho}} h(\vec{r}) - \beta \Sigma \nabla_r^2 h(\vec{r}) \right] - \nabla_r \cdot \left[\vec{\Gamma} \cdot \vec{r}\, h(\vec{r}) \right] + C(r)$$

Fourier transformation, with the neglect of the shear contribution $\nabla_r \cdot \left[\vec{\Gamma} \cdot \vec{r}\, h(\vec{r}) \right]$ using that $\nabla \rightarrow i\vec{k}$, gives,

$$0 = -2D_0\, k^2 \left[\beta \frac{d\Pi}{d\bar{\rho}} - \beta \Sigma k^2 \right] h^{eq}(k) + C(k) \qquad (1)$$

where $h^{eq}(k)$ is the Fourier transformation of $h^{eq}(r)$, where "eq" stands for "equilibrium" (that is $h(\vec{r})$ without shear flow). Now consider Fourier transformation of the shear term,

$$I(\vec{k}) \equiv -\int d\vec{r}\, e^{-i\vec{k}\bullet\vec{r}}\, \nabla_r \cdot \left[\vec{\Gamma} \cdot \vec{r}\, h(\vec{r}) \right] = -i\vec{k} \bullet \int d\vec{r}\, e^{-i\vec{k}\bullet\vec{r}} \left[\vec{\Gamma} \cdot \vec{r}\, h(\vec{r}) \right]$$

Since $\nabla_k\, e^{-i\vec{k}\bullet\vec{r}} = -i\vec{r} e^{-i\vec{k}\bullet\vec{r}}$ (with ∇_k the gradient operator with respect to $\vec{k}$)

$$I(\vec{k}) = \vec{k} \bullet \vec{\Gamma} \bullet \nabla_k \int d\vec{r}\, e^{-i\vec{k}\bullet\vec{r}}\, h(\vec{r}) = \vec{k} \bullet \vec{\Gamma} \bullet \nabla_k h(\vec{k})$$

Hence, the full differential equation for $h(\vec{k})$ in the presence of shear flow reads,

$$0 = -2D_0 \nabla_r^{\ 2} \left[\beta \frac{d\Pi}{d\bar{\rho}} + \beta \Sigma k^2 \right] h(k) + C(k) + \vec{k} \bullet \vec{\Gamma} \bullet \nabla_k h(\vec{k}) \qquad (2)$$

To eliminate the arbitrary short-ranged correlation function $C(k)$, subtract eqn. (1) from eqn. (2) ,

$$0 = -2D_0 \nabla_r^{\ 2} \left[\beta \frac{d\Pi}{d\bar{\rho}} + \beta \Sigma k^2 \right] \left(h(k) - h^{eq}(k) \right) + \vec{k} \bullet \vec{\Gamma} \bullet \nabla_k h(\vec{k})$$

Now use

$$\vec{k} \bullet \vec{\Gamma} \bullet \nabla_k = \dot{\gamma} \vec{K} \bullet \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \bullet \nabla_k = \dot{\gamma} k_1 \frac{\partial}{\partial k_2}$$

Since $S(k) = 1 + \bar{\rho}\, h(k)$, this immediately leads to,

$$\dot{\gamma} k_1 \frac{\partial}{\partial k_2} S(k) = 2 D^{eff}(k) k^2 \left(S(k) - S^{eq}(k) \right)$$

where

$$D^{eff}(k) = D_0 \beta \left[\frac{d\Pi}{d\bar{\rho}} + \Sigma k^2 \right]$$

The solution of the above equation is given in eqns. (8.50-52) in the book, and is plotted in the figure below.

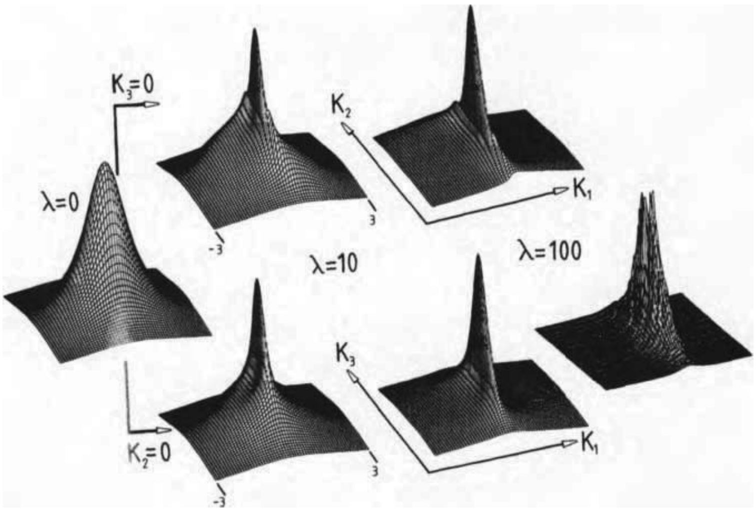


Fig. 8.11: The static structure factor as a function the wave vector components where $K_3 = 0$ (upper) and $K_2 = 0$, for the dimensionless constant $\lambda = 10,$ and

$$\frac{\beta \Sigma}{R_V^2} \left(\frac{R_V}{\xi} \right)^2 = \frac{1}{100} \quad .$$

The most left side of the figure is the equilibrium Ornstein-Zernike static structure factor, and the most right figure is an experimental scattering pattern with $K_2 = 0$.

8.4 Spinodal decomposition

The only difference with eqn. (8.45) and the appropriate equation relevant for spinodal decomposition, is that the non-stationary equation must be considered,

$$\frac{\partial}{\partial t}h(\vec{r},t|\dot{\gamma}) = 2D_0\nabla_r^{\,2}\left[\beta\frac{d\Pi}{d\bar{\rho}}h(\vec{r},t|\dot{\gamma}) - \beta\Sigma\nabla_r^{\,2}h(\vec{r},t|\dot{\gamma})\right] - \nabla_r\cdot\left[\vec{\Gamma}\cdot\vec{r}\,h(\vec{r},t|\dot{\gamma})\right]$$

Without shear flow, Fourier transformation (see also exercise 8.3) leads to,

$$\frac{\partial}{\partial t}h(\vec{k},t) = -2D^{eff}(k)k^2 h(\vec{k},t) \qquad (1)$$

with the effective diffusion coefficient is equal to,

$$D^{eff}(k) = D_0\beta\left[\frac{d\Pi}{d\bar{\rho}} + \Sigma k^2\right] \qquad (2)$$

The solution of the above eqn.(1) is,

$$h(\vec{k},t) = h(\vec{k},t=0)\exp\left(-2D^{eff}(k)k^2 t\right) \qquad (3)$$

Those wavevectors for which $D^{eff}(k) < 0$ are therefore unstable, or, from eqn. (2),

$$\frac{d\Pi}{d\bar{\rho}} + \Sigma k^2 < 0$$

Hence, all wavevectors for which,

$$\boxed{k < \sqrt{-\frac{d\Pi}{d\bar{\rho}}/\Sigma} \equiv k_c}$$

are unstable, where k_c is "the critical wavevector". Sinusoidal concentration variations with a wavelength larger than $2\pi/k_c$ will grow in amplitude, leading to decomposition.

Not all wavelengths grow equally fast. The demixing rate is, according to eqn. (2) equal to $D^{eff}(k)k^2$. The most fast growing wavevector k_m is found from,

$$\frac{d}{dk}\left[D^{eff}(k)k^2\right] = 0$$

leading to,

$$\boxed{k_m = \sqrt{-\frac{d\Pi}{d\bar{\rho}}/2\Sigma} = \frac{k_c}{\sqrt{2}}}$$

The growth rate is plotted in the figure below, for two different quenches. For a deep quench, far into the unstable part of the phase diagram, where $-d\Pi / d\overline{\rho}$ is relatively large, the growth is fast, and the fastest growing wavelength is relatively small.

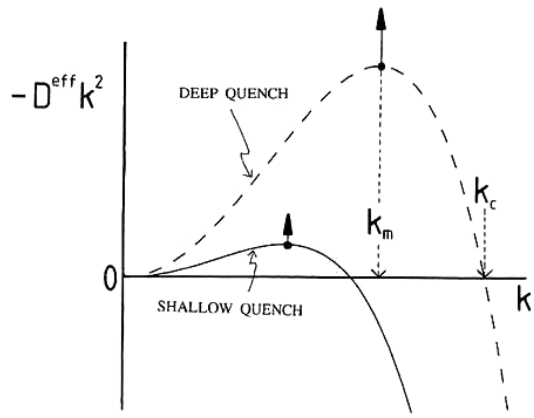


Fig. 9.4: A sketch of the growth rate of sinusoidal density variations as a function of their wavevector. The dashed curve is for a deep quench; while as the solid line is for a shallow quench.

8.5 The turbidity of an unsheared system

(a) For an unsheared system in equilibrium, the static structure factor in the integral expressing the turbidity (see eqn. (8.68) in the book),

$$\tau = C_\tau \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, P(k)\, S\left(\vec{k}\,|\dot{\gamma}\right) f\left(\theta,\varphi\right)$$

is a function of $k = \left|\vec{k}\right|$ only, where,

$$f\left(\theta,\varphi\right) = \left(\hat{n}_\theta \bullet \hat{n}_0\right)^2 + \left(\hat{n}_\phi \bullet \hat{n}_0\right)^2 = \left(\sin^2\varphi + \cos^2\varphi\cos^2\theta\right)$$

and

$$C_\tau = \frac{k_0^4}{\left(4\pi\right)^2}\bar{\rho} V_p^2 \left|\frac{\bar{\varepsilon}_p - \varepsilon_f}{\varepsilon_f}\right|^2$$

In case of $S\left(\vec{k}\right) = S^{eq}(k)$, using that,

$$\int_0^{2\pi} d\varphi\left(\sin^2\varphi + \cos^2\varphi\cos^2\theta\right) =$$

$$\int_0^{2\pi} d\varphi \sin^2\varphi + \int_0^{2\pi} d\varphi \cos^2\varphi\cos^2\theta = \frac{1}{2}\left[2\pi(1+\cos^2\theta)\right] = \pi(1+\cos^2\theta)$$

it is immediately found that,

$$\tau = \pi C_\tau \int_0^{\pi} d\theta\left(1+\cos^2\theta\right)\sin\theta\, P(k)\, S^{eq}\left(k\right) \qquad (1)$$

For small particles, away from a possible critical point, $P(k) \approx 1$ over the entire scattering angle range (this is the case when $k_0 a \le 0.5$), and furthermore $S^{eq}\left(k\right) \approx S^{eq}\left(k=0\right)$, for all scattering wave vectors. Since,

$$S^{eq}\left(k=0\right) = \frac{k_B T}{\left(\dfrac{d\Pi}{d\bar{\rho}}\right)}$$

it is found that,

$$\tau = \pi C_\tau S\left(k\right)\int_{-1}^{1} dx\left(1+x^2\right) = \frac{8\pi}{3} C_\tau\, S(k=0) = \frac{8}{3}\pi\, C_\tau \frac{k_B T}{\left(\dfrac{d\Pi}{d\bar{\rho}}\right)} \qquad (2)$$

This equation offers the possibility to characterize the pair-interaction potential for small particles by means of turbidity measurements, since according to,

$$\Pi = \bar{\rho} k_B T - \frac{2\pi}{3}\bar{\rho}^2 \int_0^{\infty} dr' \, r'^3 \frac{dV(r')}{dr'} g(r')$$

the second order in concentration expansion of the osmotic pressure is given by

$$\Pi = \bar{\rho} k_B T + \frac{2\pi}{3} \bar{\rho}^2 k_B T \int_0^\infty dr' r'^3 \frac{d \exp(-\beta V(r'))}{dr'}$$

This expression can be explicitly evaluated for a square-well potential, superimposed on a hard-core potential, which is defined as,

$$V(r') = \begin{cases} \infty, & r' < 2a \\ -\varepsilon, & 2a \le r' < 2a + \Delta \\ 0, & r' \ge 2a + \Delta \end{cases}$$

where ε is the depth of the attractive well, and Δ is the range of the attractive interaction potential. We now have,

$$e^{-\beta V(r')} = \begin{cases} 0, & r' < 2a \\ e^{\beta \varepsilon}, & 2a \le r' < 2a + \Delta \\ 1, & r' \ge 2a + \Delta \end{cases}$$

so that,

$$\frac{d \exp(-\beta V(r'))}{dr'} = e^{\beta \varepsilon} \delta(r' - 2a) - \left(e^{\beta \varepsilon} - 1\right) \delta(r' - 2a - \Delta)$$

where δ is the delta function. The delta functions allow for the explicit evaluation of the integral,

$$\begin{aligned} \Pi &= \bar{\rho} k_B T + \frac{2\pi}{3} \bar{\rho}^2 k_B T \int_0^\infty dr' r'^3 \left[e^{\beta \varepsilon} \delta(r' - 2a) - \left(e^{\beta \varepsilon} - 1\right) \delta(r' - 2a - \Delta) \right] \\ &= \bar{\rho} k_B T + \frac{2\pi}{3} \bar{\rho}^2 k_B T \left[(2a)^3 e^{\beta \varepsilon} - (2a + \Delta)^3 \left(e^{\beta \varepsilon} - 1\right) \right] \end{aligned}$$

For $\frac{\Delta}{2a} \ll 1$, this reduces to,

$$\Pi \simeq \bar{\rho} k_B T + \frac{2\pi}{3} \bar{\rho}^2 k_B T (2a)^3 \left[1 + \left(1 - e^{\beta \varepsilon}\right) \frac{3\Delta}{2a} \right]$$

We can now take the "sticky-sphere limit", where $\varepsilon \to \infty$, $\Delta \to 0$ such that,

$$\alpha = 12 \lim_{\substack{\varepsilon \to \infty \\ \Delta \to 0}} \left[\exp(\beta \varepsilon) - 1 \right] \frac{\Delta}{a} \quad \to \quad \textit{finite}$$

Hence,

$$\boxed{\lim_{\substack{\Delta \to 0 \\ \Sigma \to \infty}} \left(1 - e^{\beta \varepsilon}\right) \frac{3\Delta}{2a} = -\frac{1}{8} \alpha}$$

so that,

$$\Pi \simeq \bar{\rho} k_B T + \frac{2\pi}{3} \bar{\rho}^2 (2a)^3 k_B T \left[1 - \frac{1}{8}\alpha\right]$$

and hence,

$$\left(\frac{d\Pi}{d\bar{\rho}}\right) = k_B T + 8\varphi k_B T \left[1 - \frac{1}{8}\alpha\right]$$

It is finally found from eqn. (2) that,

$$\boxed{\tau^{eq} = C_\tau \frac{8\pi}{3} \left[1 - (8 - \alpha)\varphi\right]}$$

up to order φ^2 where $\varphi = \frac{4\pi}{3} a^3 \bar{\rho}$ is the volume fraction. Note that this result is actually correct up to order φ^3, since $C_\tau \sim \bar{\rho} \sim \varphi$.

This equation applies to the colloidal system consisting of silica particles coated with stearyl alcohol chains and dissolved in benzene, whose phase diagram is shown in Fig.8.1. Turbidity measurements on dilute samples can be employed to characterize the pair-interaction potential of these particles through the single parameter α.

(b) Near the critical point, $S^{eq}(k) \neq S^{eq}(k=0)$, contrary to the case considered in (a) for a system of small particles. According to eqn. (8.36) we now have,

$$S(k) = \frac{1}{\beta\Sigma} \frac{\xi^2}{1 + (k\xi)^2} \quad \text{for} \quad k \ll \frac{2\pi}{R_V}.$$

Using this in eqn.(1) for the turbidity gives,

$$\tau = \pi C_\tau \int_0^\pi d\theta \left(1 + \cos^2\theta\right) \sin\theta \, P(k) \, S(k)$$

$$= \pi C_\tau \frac{\xi^2}{\beta\Sigma} \int_0^\pi d\theta \left(1 + \cos^2\theta\right) \sin\theta \, \frac{1}{1 + (k\xi)^2}$$

where it is again assumed that the particles are sufficiently small to set the form factor equal to unity. Introducing the new integration variable,

$$k = \frac{4\pi}{\lambda_n} \sin\left(\frac{\theta}{2}\right) = 2k_0 \sin\left(\frac{\theta}{2}\right)$$

where $k_0 = 2\pi / \lambda_n$, and hence, $dk = k_0 \cos\left(\frac{\theta}{2}\right) d\theta$

using that,

$$\sin\theta = 2\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right), \quad \cos\theta = \cos^2\left(\frac{\theta}{2}\right) - \sin^2\left(\frac{\theta}{2}\right), \quad \cos^2\left(\frac{\theta}{2}\right) = 1 - \sin^2\left(\frac{\theta}{2}\right)$$

the integral reads,

$$\boxed{\tau = \pi C_\tau \frac{\xi^2}{\beta\Sigma k_0^{\,2}} \int_0^{2k_0} dk \; \frac{k}{1+(k\xi)^2}\left[2 - \left(\frac{k}{k_0}\right)^2 + \frac{1}{4}\left(\frac{k}{k_0}\right)^4\right]}$$

The integral can be conveniently rewritten, once more, by introducing the yet new integration variable $x = (k/2k_0)^2$, leading to,

$$\tau = \pi C_\tau \frac{1}{2\beta\Sigma k_0^{\,2}} \; z^2 \int_0^1 dx \; \frac{\left[2 - 4x + 4x^2\right]}{1 + x\,z^2}$$

where $z = 2k_0\xi$. The integral is evaluated using the standard integrals,

$$\int dx \; \frac{1}{1+x\,z^2} = \frac{1}{z^2}\ln\left(1 + x\,z^2\right)$$

$$\int dx \; \frac{x}{1+x\,z^2} = \frac{x}{z^2} - \frac{1}{z^4}\ln\left(1 + x\,z^2\right)$$

$$\int dx \; \frac{x^2}{1+x\,z^2} = \frac{1}{z^6}\left[\frac{1}{2}\left(1 + x\,z^2\right)^2 - 2\left(1 + x\,z^2\right) + \ln\left(1 + x\,z^2\right)\right]$$

it follows that

$$\boxed{\tau = C_\tau \frac{\pi}{2\beta\Sigma k_0^{\,2}} \; G(2k_0\xi)}$$

where

$$\boxed{G(z) = -\frac{4+2z^2}{z^2} + \frac{4+4z^2+2z^4}{z^4}\ln\{1+z^2\}}$$

8.6 Self-diffusion near the critical point

According to eqn. (6.49), the short-time self-diffusion coefficient is given by,

$$D_S^S = D_0 \left\{ 1 + \varphi \int_2^\infty dx\, x^2\, g\left(ax\right)\left[A_S\left(ax\right) + 2B_S\left(ax\right) \right] \right\} \qquad (1)$$

where, according to eqn. (6.46), the leading order terms of the hydrodynamic interaction functions are,

$$A_S\left(r_{1j}\right) = -\frac{15}{4}\left(\frac{a}{r_{1j}}\right)^4 + \frac{11}{2}\left(\frac{a}{r_{1j}}\right)^6,$$

$$B_S\left(r_{1j}\right) = -\frac{17}{16}\left(\frac{a}{r_{1j}}\right)^6$$

Note that $x = \left(\frac{a}{r_{1j}}\right)$ in eqn (1). According to eqn. (8. 12),

$$g(r) - 1 = \left(AR_V\right)\frac{\exp\left(-r/\xi\right)}{r}, \quad \text{for} \quad r \gg R_V$$

where, according to eqn. (8.15),

$$\left(AR_V\right) = \frac{1}{4\pi\,\bar{\rho}}\frac{1}{\xi^2}\left[\left(\beta\frac{d\Pi}{d\bar{\rho}}\right)^{-1} - 1\right] \approx \frac{1}{4\pi\,\bar{\rho}}\frac{1}{\xi^2}\left(\beta\frac{d\Pi}{d\bar{\rho}}\right)^{-1}$$

Close to the critical point, $\beta d\Pi / d\bar{\rho} \ll 1$, and

$$\left(\beta\frac{d\Pi}{d\bar{\rho}}\right)^{-1} = \frac{\xi^2}{\beta\Sigma}$$

so that the pair-correlation function can also be written as,

$$g(r) = 1 + \frac{1}{4\pi\,\bar{\rho}\beta\Sigma}\frac{\exp\left(-r/\xi\right)}{r}$$

or, in terms of the integration variable $x = r/a$ in eqn.(1),

$$g(ax) = 1 + \frac{1}{4\pi\,\bar{\rho}a\beta\Sigma}\frac{\exp\left(-xa/\xi\right)}{x}$$

It follows that,

$$\boxed{\begin{aligned} D_S^S &= D_0\left\{1-\frac{15}{4}\varphi\int_2^\infty dx\,x^{-2}-\frac{15}{4}\varphi\left(\frac{1}{4\pi\bar{\rho}\,a\beta\Sigma}\right)\int_2^\infty dx\,x^{-3}\exp\left(-xa/\xi\right)\right\} \\ &= D_0\left\{1-1.88\varphi-\frac{5}{4}\frac{1}{\beta\Sigma/a^2}H(a/\xi)\right\}, \end{aligned}}$$

where

$$H(a/\xi)=\int_2^\infty dx\frac{\exp\left(-ax/\xi\right)}{x^3}$$

At the critical point, $\xi\to\infty$, and hence

$$\boxed{H(a/\xi=z)\to\int_2^\infty dx\frac{1}{x^3}=\frac{1}{8}}$$

So that the short-time self diffusion coefficient D_S^S is well-behaved at the critical point.

*** Perform a partial integration, $\int dz\,f\,g'=f\,g\big|-\int dz\,f'g$

and use,

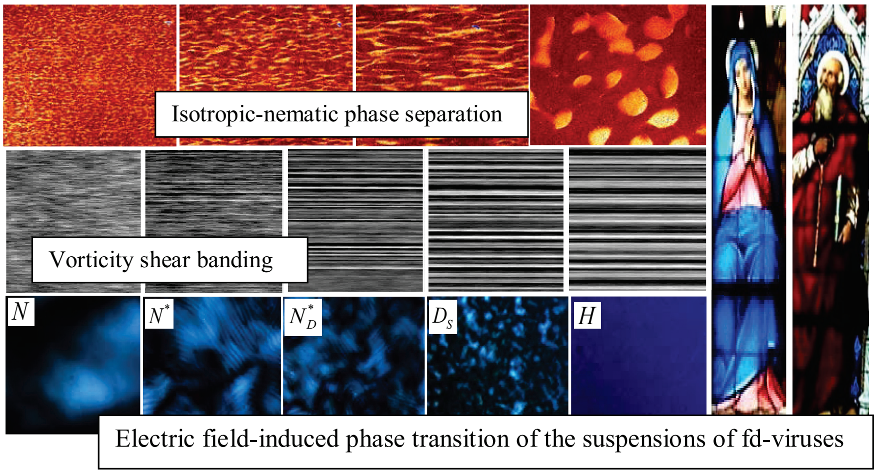
$$\int dx\frac{e^{ax}}{x^n}=\frac{1}{n-1}\left(-\frac{e^{ax}}{x^{n-1}}+a\int dx\frac{e^{ax}}{x^{n-1}}\right),\quad n\neq 1$$

$$\int dx\frac{e^{ax}}{x}=\ln x+\frac{ax}{1*1!}+\frac{(ax)^2}{2*2!}+\frac{(ax)^3}{3*3!}+\cdots$$

to find that,

$$\begin{aligned} \int_2^\infty dx\frac{e^{-zx}}{x^3} &= \frac{1}{2}\left(-\frac{e^{-zx}}{x^2}\bigg|_{x=2}^{\infty}-z\int_2^\infty dx\frac{e^{-zx}}{x^2}\right)=\frac{1}{2}\frac{e^{-2z}}{4}-\frac{z}{2}\left(\left(-\frac{e^{-zx}}{x}\bigg|_{x=2}^{\infty}-z\int_2^\infty dx\frac{e^{-zx}}{x}\right)\right) \\ &= \frac{e^{-2z}}{8}-\frac{z\,e^{-2z}}{4} \\ &\quad +\frac{z^2}{2}\int_2^\infty dx\frac{e^{-zx}}{x}=\frac{e^{-2z}}{8}-\frac{z\,e^{-2z}}{4}+\frac{z^2}{2}\left(\ln x-\frac{zx}{1*1!}+\frac{(zx)^2}{2*2!}-\frac{(zx)^3}{3*3!}+\cdots\right)_{x=2}^{\infty}\simeq\frac{1}{8} \end{aligned}$$

Exercise Chapter 9: PHASE SEPARATION



9.1 Stability and decomposition kinetics of a van der Waals fluid

(a) For a homogeneous system, $N_j = N\dfrac{\Delta}{V}$ is independent of the "box- numbering index " j .

Hence, from eqns. (9.105) and (9.106),

$$A = -k_B T \sum_j \left\{ N\frac{\Delta}{V}\ln\left(\Delta - N\frac{\Delta}{V}\delta\right) - N\frac{\Delta}{V}\ln\left(N\frac{\Delta}{V}\right) + N\frac{\Delta}{V}\right\} + \frac{1}{2}\frac{N^2}{V^2}\sum_{i,j} w_{ij}\Delta^2$$

Since
$$\left(\sum_j const\right) = const*\left(number\ of\ boxes\right) = const*\left(\frac{V}{\Delta}\right)$$

and (with $\vec{R} = \vec{r} - \vec{r}\,'$) this can be written as,

$$\sum_{i,j} w_{ij}\Delta^2 = \int_{r>d} d\vec{r} \int_{r>d} d\vec{r}\,' w\left(\left|\vec{r} - \vec{r}\,'\right|\right) = V\int_{r>d} d\vec{R}\, w\left(R\right) = 4\pi V \int_{R>d}^{\infty} dR\, R^2 w(R)$$

where, by definition,

$$A = -k_B T\, N\left(1 + \ln\left(\frac{V - N\delta}{N}\right)\right) - \frac{1}{2}\frac{N^2}{V} w_0$$

The osmotic pressure Π is equal to,

$$w_0 = -4\pi V \int_{R>d}^{\infty} dR\, R^2 w(R) > 0$$

which represents the van der Waals equation of state.

$$\boxed{\Pi = -\frac{\partial A\left(N,V,T\right)}{\partial V} = k_B T \frac{\bar{\rho}}{1 - \bar{\rho}\,\delta} - \frac{1}{2}\bar{\rho}^2 w_0}$$

(b) We start with the condition that the homogeneous system is (spinodaly) unstable,

$$\frac{\partial \Pi(\bar{\rho},T)}{\partial \bar{\rho}} < 0$$

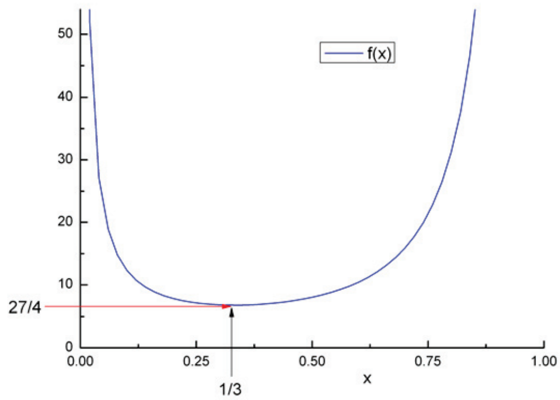
Differentiation of the osmotic pressure Π , as derived in (a), leads to,

$$\frac{d\Pi}{d\bar{\rho}} = \frac{k_B T}{(1-\bar{\rho}\,\delta)^2} - \bar{\rho} w_0 < 0 \qquad (1)$$

or, with $x = \bar{\rho}\,\delta$ (is a “volume fraction”, which varies between 0 and 1),

$$\frac{\beta w_0}{\delta} > \frac{1}{x\left(1-x\right)^2}$$

The function $f(x) \equiv \dfrac{1}{x\left(1-x\right)^2}$ is plotted below. The minimum value of this function is $27/4$.



It follows that there is no unstable state when $\dfrac{\beta w_0}{\delta} < \dfrac{27}{4}$. The critical temperature T_c is the temperature for which $\dfrac{\beta w_0}{\delta} = \dfrac{27}{4}$, hence, $T_c = \dfrac{27}{4}\dfrac{w_0}{k_B \delta}$.

For temperatures below this critical temperature, the system can be unstable

(b) In a "small" box (numbering j), the volume fraction of spheres is proportional to $\varphi_j \equiv N_j \delta / \Delta$, where δ is four times the core volume of a particle, Δ is the volume of the box, and N_j is the number of spheres in a box j. Eqn (9.105) reads in terms of φ_j,

$$\Psi(\vec{r}_1, \cdots, \vec{r}_N) = -\frac{k_B T}{\delta} \Delta \sum_j \left\{ \varphi_j \left[\ln \Delta + \ln(1-\varphi_j) \right] - \varphi_j \left[\ln \Delta - \ln \delta + \ln \varphi_j \right] + \varphi_j \right\}$$
$$+ \frac{1}{2} \left(\frac{\Delta}{\delta} \right)^2 \sum_{i,j} w_{ij}\, \varphi_i \varphi_j$$

or,

$$\Psi(\vec{r}_1, \cdots, \vec{r}_N) = -\frac{k_B T}{\delta} \Delta \sum_j \varphi_j \left[\ln \left(\frac{1-\varphi_j}{\varphi_j} \right) + \ln \delta + 1 \right] + \frac{1}{2} \left(\frac{\Delta}{\delta} \right)^2 \sum_{i,j} w_{ij}\, \varphi_i \varphi_j$$

The boxes are on the one-hand large enough to contain many particles, in order that each box can be considered as a thermodynamic system, and on the other hand are small enough that φ_j's change is only little between adjacent boxes.

The first requirement allows to equate the function $\Psi(\vec{r}_1, \cdots, \vec{r}_N)$ to the free energy $A[\varphi(\vec{r})]$ of the inhomogeneous system, while the second requirement allows to replace sums by integrals, where $\vec{r}$ plays the role of the box-number index j,

$$\sum_j \Delta f_j \equiv \int d\vec{r}\; f(\vec{r})$$

for well-behaved functions *f*. Hence, the free energy can be written as,

$$A[\varphi(\vec{r})] = -\frac{k_B T}{\delta} \int d\vec{r}\, \varphi(\vec{r}) \left[\ln \left(\frac{1-\varphi(\vec{r})}{\varphi(\vec{r})} \right) + \ln(\delta) + 1 \right]$$
$$+ \frac{1}{2\delta^2} \int d\vec{r} \int d\vec{r}\,'\; w(|\vec{r} - \vec{r}\,'|)\, \varphi(\vec{r}\,') \varphi(\vec{r})$$

By taking $\varphi(\vec{r}) \rightarrow \varphi(\vec{r}) + \delta\varphi(\vec{r})$, with $\delta\varphi(\vec{r})$ a small variation of the volume fraction, we thus have, upon expanding the first order in $\delta\varphi(\vec{r})$,

$$A[\varphi(\vec{r}) + \delta\varphi(\vec{r})] = A[\varphi(\vec{r})] - \frac{k_B T}{\delta} \int d\vec{r}\, \delta\varphi(\vec{r}) \left[\ln \left(\frac{1-\varphi(\vec{r})}{\varphi(\vec{r})} \right) - \frac{1}{1-\varphi(\vec{r})} + \ln(\delta) + 1 \right]$$
$$+ \frac{1}{2\delta^2} \int d\vec{r} \int d\vec{r}\,'\; w(|\vec{r} - \vec{r}\,'|) \left[\varphi(\vec{r}\,') \delta\varphi(\vec{r}) + \varphi(\vec{r}) \delta\varphi(\vec{r}\,') \right]$$

Since

$$\int d\vec{r} \int d\vec{r}\,'\; w(|\vec{r} - \vec{r}\,'|)\, \varphi(\vec{r}\,') \delta\varphi(\vec{r}) = \int d\vec{r} \int d\vec{r}\,'\; w(|\vec{r} - \vec{r}\,'|)\, \varphi(\vec{r}) \delta\varphi(\vec{r}\,')$$

It follows, by definition, that,

$$\frac{\delta A\left[\varphi(\vec{r})\right]}{\delta\varphi(\vec{r})}=-\frac{k_BT}{\delta}\left[\ln\left(\frac{1-\varphi(\vec{r})}{\varphi(\vec{r})}\right)-\frac{1}{1-\varphi(\vec{r})}+\ln(\delta)+1\right]$$
$$+\frac{1}{\delta^2}\int d\vec{r}\,'\;w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\varphi(\vec{r}\,')$$

Hence, the chemical potential is equal to,

$$\mu(\vec{r})=\frac{\delta A\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}=\frac{\delta A\left[\varphi(\vec{r})\right]}{\delta\varphi(\vec{r})}*\delta$$
$$=-k_BT\left[\ln\left(\frac{1-\varphi(\vec{r})}{\varphi(\vec{r})}\right)-\frac{1}{1-\varphi(\vec{r})}+\ln(\delta)+1\right]+\frac{1}{\delta}\int d\vec{r}\,'\;w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\varphi(\vec{r}\,')$$

The mass flux is in turn equal to,

$$\vec{j}=-D\nabla\mu(\vec{r})$$
$$=Dk_BT\,\nabla\varphi(\vec{r})\frac{\partial}{\partial\varphi(\vec{r})}\left[\ln\left(\frac{1-\varphi(\vec{r})}{\varphi(\vec{r})}\right)-\frac{1}{1-\varphi(\vec{r})}+\ln(\delta)+1\right]$$
$$-\frac{D}{\delta}\int d\vec{r}\,'\left[\nabla w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\right]\varphi(\vec{r}\,')$$
$$=-Dk_BT\frac{1}{\varphi(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\nabla\varphi(\vec{r})+\frac{D}{\delta}\int d\vec{r}\,'\left[\nabla' w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\right]\varphi(\vec{r}\,')$$

The equation of motion for $\varphi(\vec{r})$ is thus (here we also denote the time dependence of $\varphi(\vec{r})$ explicitly) as,

$$\frac{\partial\varphi(\vec{r},t)}{\partial t}=-\delta\nabla\bullet\vec{j}(\vec{r},t)$$
$$=Dk_BT\delta\left\{\left[\nabla\left(\frac{1}{\varphi(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\right)\right]\bullet\nabla\varphi(\vec{r})+\left(\frac{1}{\varphi(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\right)\nabla^2\varphi(\vec{r})\right\}$$
$$-D\int d\vec{r}\,'\left[\nabla' w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\right]\varphi(\vec{r}\,',t)$$

$$=-Dk_BT\delta\frac{1-4\varphi(\vec{r},t)+3\varphi^2(\vec{r},t)}{\varphi^2(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\left|\nabla\varphi(\vec{r},t)\right|^2$$
$$+Dk_BT\delta\frac{1}{\varphi^2(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\nabla^2\varphi(\vec{r},t)-D\int d\vec{r}\,'\;w\left(\left|\vec{r}-\vec{r}\,'\right|\right)\nabla'^2\varphi(\vec{r}\,',t)$$

In the last term, we used Gauss's integral theorem twice. Now consider the initial stage of spinodal decompositions, we write,

$$\varphi(\vec{r},t) = \bar{\varphi} + \delta\varphi(\vec{r},t)$$

with $\bar{\varphi}$ the volume fraction of the initially homogeneous system, and $\delta\varphi(\vec{r},t)$ is the small deviation from homogeneity due to demixing. Substituting into the above the equation of motion, and linearization with respect to $\delta\varphi(\vec{r},t)/\bar{\varphi}$, leads to,

$$\frac{\partial}{\partial t}\delta\varphi(\vec{r},t) = Dk_B T\delta \frac{1}{\varphi(\vec{r})\left(1-\varphi(\vec{r})\right)^2}\nabla^2\delta\varphi(\vec{r},t) + D\int d\vec{r}\,'\; w(|\vec{r}-\vec{r}\,'|)\nabla'^2\,\delta\varphi(\vec{r}\,',t)$$

Note that $|\nabla\delta\varphi(\vec{r},t)|^2$ is of second order, so that the first term in the original equation of motion does not contribute.

The Fourier transform of $\nabla^2\delta\varphi(\vec{r},t)$ is equal to $-k^2\delta\varphi(\vec{k},t)$ (with $\vec{k}$ the Fourier variable), while the integral is a convolution integral, so that its Fourier transform is equal to,

$$FT\left[\int d\vec{r}\,'\; w(|\vec{r}-\vec{r}\,'|)\nabla'^2\,\delta\varphi(\vec{r}\,',t)\right] = -\omega(k)k^2\,\delta\varphi(\vec{k},t),$$

where

$$\omega(k) = \int d\vec{r}\;\; w(r)e^{-i\vec{k}\cdot\vec{r}}$$

is the Fourier transform of $\omega(r)$. Hence

$$\frac{\partial}{\partial t}\delta\varphi(\vec{k},t) = -D\,k^2\left[\frac{k_B T\delta}{\bar{\varphi}(1-\bar{\varphi})^2} + \omega(k)\right]\delta\varphi(\vec{k},t)$$

Introducing the "effective diffusion coefficient" as,

$$D^{eff}(k) \equiv D\left[\frac{k_B T\delta}{\bar{\varphi}(1-\bar{\varphi})^2} + \omega(k)\right]$$

The solution of this simple linear equation of motion reads to,

$$\delta\varphi(\vec{k},t) = \delta\varphi(\vec{k},t=0)\exp\left[-D^{eff}(k)\,k^2 t\right]$$

For the small spatial gradients that are present during the initial stage of spinodal decomposition, it is sufficient to expand $\omega(k)$ up to $O(k^2)$,

$$\omega(k) = \int d\vec{r}\; w(r)e^{-i\vec{k}\cdot\vec{r}} \simeq \int d\vec{r}\; w(r)\left[1 - i\vec{k}\cdot\vec{r} - \frac{1}{2}\left(\vec{k}\cdot\vec{r}\right)^2\right] \equiv -\omega_0 + k^2\omega_2$$

where $\hat{k} = \frac{\vec{k}}{k}$ is the unit vector along the wavevector $\vec{k}$, and $\hat{I}$ is the identity tensor, and,

$$\omega_0 \equiv -\int d\vec{r} w(r) = -4\pi \int_0^\infty dr\, r^2 w(r)$$

$$\omega_2 \equiv -\frac{1}{2}\hat{k}\,\hat{k} : \int d\vec{r}\, \vec{r}\, \vec{r}\, w(r) = -\frac{1}{2}\hat{k}\,\hat{k} : \frac{4\pi}{3}\hat{I}\int_0^\infty dr\, r^4 w(r) = -\frac{2\pi}{3}\int_0^\infty dr\, r^4 w(r)$$

Note that $\omega_0, \omega_2 > 0$, since $w(r) < 0$, being an attractive potential. The effective diffusion coefficient for small spatial gradients is thus equal to,

$$\boxed{D^{eff}(k) \equiv D\left[\frac{k_B T \delta}{\overline{\varphi}(1-\overline{\varphi})^2} - \omega_0 + k^2 \omega_2\right]}$$

Hence, $D^{eff}(k=0) < 0$, when $\omega_0 > \frac{k_B T \delta}{\overline{\varphi}(1-\overline{\varphi})^2}$, or, since $\overline{\varphi} = \overline{\rho}\,\delta$ (with $\overline{\rho}$ the number density of the homogeneous system),

$$\omega_0 > \frac{k_B T}{\overline{\rho}(1-\overline{\rho}\delta)^2}$$

which reproduces the criterion eqn (9.107). Since $D / D_0 = \beta\,\overline{\rho}$, it follows that,

$$D^{eff}(k=0) = D_0 \beta \left[\frac{k_B T}{(1-\overline{\rho}\delta)^2} - \omega_0 \overline{\rho}\right]$$

The term between the brackets is equal to $\partial\Pi / \partial\overline{\rho}$ (see eqn.(1) for the osmotic pressure), so that,

$$D^{eff}(k=0) = D_0 \beta \frac{\partial \Pi}{\partial \overline{\rho}}$$

in accordance with the general expression in eqn (9.28). Comparing the general expression (9.28) for the effective diffusion coefficient shows that,

$$D_0 \beta \Sigma = D\omega_2 = D_0 \beta\, \overline{\rho}\, \omega_2$$

and hence,

$$\boxed{\Sigma = \overline{\rho}\, \omega_2 > 0}$$

9.2 Fourier transformation of the Smoluchowski equation with respect to the displacement gives

$$F.T.\left\{\frac{\partial}{\partial t}\delta\rho\left(\vec{r},t\right)=D_0\left[\begin{array}{l}\nabla^2\delta\rho\left(\vec{r},t\right)+\beta\,\bar{\rho}\nabla\bullet\int d\vec{R}\left(\nabla_R V\left(R\right)\right)\\ \quad *\left(g(R)\delta\rho\left(\vec{r}-\vec{R},t\right)+\bar{\rho}\dfrac{dg^{eq}(R)}{d\bar{\rho}}\delta\rho\left(\vec{r}-\dfrac{1}{2}\vec{R},t\right)\right)\end{array}\right]\right\} \qquad (1)$$

gives rise to the integral,

$$I\left(\vec{k}\right)\equiv i\vec{k}\cdot\int d\vec{r}\int d\vec{R}\left[\nabla_R V\left(R\right)\right]f(R)\;\delta\rho\left(\vec{r}-\alpha\vec{R},t\right)e^{-i\vec{k}\bullet\vec{r}},\quad \alpha=1,\frac{1}{2}$$

This integral is calculated as follows,

$$\begin{aligned}I\left(\vec{k}\right)&\equiv i\vec{k}\cdot\int d\vec{r}\int d\vec{R}\left[\nabla_R V\left(R\right)\right]f(R)\;\delta\rho\left(\vec{r}-\alpha\vec{R},t\right)e^{-i\vec{k}\bullet(\vec{r}-\alpha\vec{R})}\;e^{-i\alpha\vec{k}\bullet\vec{R}}\\&=i\vec{k}\cdot\int d\vec{R}\left[\nabla_R V\left(R\right)\right]f(R)\,e^{-i\alpha\vec{k}\bullet\vec{R}}\int d\left(\vec{r}-\alpha\vec{R}\right)\delta\rho\left(\vec{r}-\alpha\vec{R},t\right)e^{-i\vec{k}\bullet(\vec{r}-\alpha\vec{R})}\\&=\delta\rho\left(\vec{k},t\right)i\vec{k}\cdot\int d\vec{R}\left[\nabla_R V\left(R\right)\right]f(R)\,e^{-i\alpha\vec{k}\bullet\vec{R}}\end{aligned}$$

Now use that

$$\left[\nabla_R V\left(R\right)\right]=\hat{R}\frac{dV(R)}{dR},\quad \hat{R}=\frac{\vec{R}}{R}$$

so that,

$$\begin{aligned}&i\vec{k}\cdot\int d\vec{R}\left[\nabla_R V\left(R\right)\right]f(R)\,e^{-i\alpha\vec{k}\bullet\vec{R}}\\&\quad=i\vec{k}\cdot\int_0^\infty dR\,R^2\frac{dV(R)}{dR}f(R)\oint d\hat{R}\,\hat{R}e^{-i\alpha\vec{k}\bullet\hat{R}R}\\&\quad=i\vec{k}\int_0^\infty dR\,R^2\frac{dV(R)}{dR}f(R)\frac{1}{-i\alpha R}\nabla_k\oint d\hat{R}\,e^{-i\alpha\vec{k}\bullet\hat{R}R}\\&\quad=i\vec{k}\cdot\int_0^\infty dR\,R^2\frac{dV(R)}{dR}f(R)\frac{1}{-i\alpha R}\nabla_k\left(4\pi\frac{\sin\alpha kR}{\alpha kR}\right)\\&\quad=i\vec{k}\cdot\int_0^\infty dR\,R^2\frac{dV(R)}{dR}f(R)\frac{1}{-i\alpha R}\alpha^2R^2\vec{k}\left(4\pi\,j(\alpha kR)\right)\end{aligned}$$

where ∇_k is the gradient operator with respect to $\vec{k}$, and,

$$j\left(x\right)\equiv\frac{x\cos\left(x\right)-\sin\left(x\right)}{x^3}$$

The integral thus reads,

$$I(\vec{k}) = -\delta\rho\left(\vec{r},t\right) 4\pi\alpha\, k^2 \int_0^\infty dR\, R^2 \frac{dV(R)}{dR} f(R)\, j(\alpha k R)$$

Using this result in eqn.(1) leads to,

$$\boxed{\begin{aligned} &\frac{\partial}{\partial t}\delta\rho\left(\vec{k},t\right) = -D^{eff}\left(k\right) k^2\, \delta\rho\left(\vec{k},t\right), \\ &D^{eff}\left(k\right) = D_0\left[1 + 2\pi\beta\,\bar{\rho}\int_0^\infty dR\, R^3 \frac{dV(R)}{dR}\left(2g^{eq}(R)\, j\left(kR\right) + \bar{\rho}\,\frac{dg^{eq}(R)}{d\bar{\rho}}\, j\left(\frac{1}{2}kR\right)\right)\right]\end{aligned}}$$

As explained in the book, expanding the (Bessel) *j*-functions with respect to the wave vector reproduces the classic Cahn-Hilliard theory for initial spinodal decomposition.

9.4 Stability and demixing of confined suspensions

Consider a rectangular box where the sides have a length L. The question is at which temperature the system becomes unstable, as compared to a system of infinite extent. The criterion for instability is unchanged, and reads,

$$D^{eff}(k) = D_0 \beta \left[\frac{d\Pi}{d\bar{\rho}} + \Sigma k^2 \right] < 0$$

Since the maximum wavelength that fits into the box is L, the minimum wave vector is $k_{\min} = 2\pi / L$. The system contained in the rectangular container therefore becomes unstable when,

$$\frac{d\Pi}{d\bar{\rho}} < -\Sigma k_{\min}^2 = -\Sigma \left(\frac{2\pi}{L} \right)^2 \qquad (1)$$

It is thus not sufficient that $d\Pi / d\bar{\rho} < 0$, like for an infinite system, but $d\Pi / d\bar{\rho}$ should be sufficiently negative before the system becomes unstable in a system of finite extent. For an upper critical point, the temperature where the system becomes unstable in a system of finite extent is therefore lower as compared to a system of infinite extent. The critical temperature and the spinodal will therefore be lowered due to confinement.

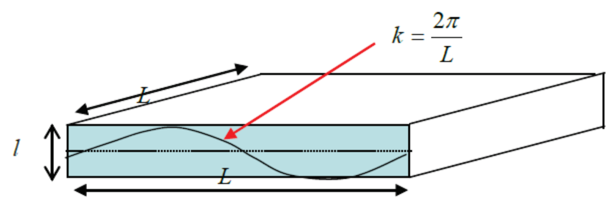
Next, consider a square flat container (as depicted in the figure), with two long sides of length L and a small side of length l, with $L \gg l$ .In such a case, upon slowly cooling, spinodal decomposition will occur first along the long dimension, when the instability condition in eqn.(1) is fulfilled.

Similarly, spinodal decomposition in the direction of the shorter distance occur when,

$$\frac{d\Pi}{d\bar{\rho}} < -\Sigma \left(\frac{2\pi}{l} \right)^2$$

Note that spinodal decomposition occurs only along the longer dimensions when,

$$-\Sigma \left(\frac{2\pi}{l} \right)^2 < \frac{d\Pi}{d\bar{\rho}} < -\Sigma \left(\frac{2\pi}{L} \right)^2$$



9.5 Porod's law

The scattered intensity from an assembly of polydisperse and optically homogeneous spheres is proportional to,

$$I(k) \sim \int_0^\infty da\, P_0(a) \left(\frac{ka\cos(ka) - \sin(ka)}{(ka)^3} \right)^2$$

where $P_0(a)$ is the distribution of the radius a of the spheres. For large wave vectors, where $ka \gg 1$, one can approximate,

$$\frac{ka\cos(ka) - \sin(ka)}{(ka)^3} \approx \frac{\cos(ka)}{(ka)^2}$$

in the integral. Hence,

$$I(k) \sim \int_0^\infty da\, P_0(a) \left(\frac{ka\cos(ka) - \sin(ka)}{(ka)^3} \right)^2$$
$$\approx k^{-4} \int_0^\infty da\, a^{-4} P_0(a)\ \cos^2(ka)$$

For wave vectors which are such that $k\sigma \gg 1$, with σ the width of the size distribution, we have,

$$\int_0^\infty da\ a^{-4} P_0(a) \cos^2(ka) \approx \int_0^\infty da\ a^{-4} P_0(a) \sin^2(ka)$$

so that,

$$I(k) \sim k^{-4} \frac{1}{2} \int_0^\infty da\ a^{-4} P_0(a) \left[\cos^2(ka) + \sin^2(ka) \right]$$

and hence,

$$\boxed{I(k) \sim k^{-4} < a^{-4} >}$$

This is the famous Porod's law that describes the scattering of sharp interfaces for large wave vectors.

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